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THE DEVELOPMENT OF COLLOID CHEMISTRY.*

BY

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WHEN considering the development of any subject chronologically, it is usually satisfactory to distinguish historical periods, even though these may, and do, overlap both in time and space. One gets a much better perspective if one makes up one's mind whether any particular, distinguished, scientific man should be classed with the sharks and the gingko trees, as a survival of a prehistoric era, or whether he is to be classed with the composite flowers, like the dandelion, which are to possess the earth.

In chemistry the early or primitive science was essentially descriptive. People made iron long ago, but they did not care about the theory of the process. If one reads the scientific literature of preceding centuries (in a translation), one learns about the discovery of Glauber's salt, of Scheele's green, and of Prussian blue. Even as recently as Faraday's time, his discovery of benzene differed only in its consequences from the discovery of Glauber's salt.

The next period was the development of the atomic and molecular theory with the law of the constant composition of compounds and the determination of atomic weights. There is no longer the thrill about this type of work that there once was,

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but it still attracts the attention of those skilful enough to make measurements with the necessary accuracy and it has acquired a new interest, temporarily, through the discovery of isotopes.

The third period is that of organic chemistry; Wöhler and Kékulé in Germany, Gerhardt in France, and van't Hoff in Holland are some of the great names in this period which gave us constitutional formulas in general, the benzene formula, and the theory of asymmetric carbon.

The fourth period is that of thermodynamics, with Carnot, Clausius, Kelvin, Helmholtz, Horstmann, Gibbs, J. J. Thomson, Ostwald, Planck, and Nernst as the important names. It is rather a question whether one should consider this as a period at all, because the early portion of it was entirely physics. I was rather surprised to find that J. P. Cooke in 1872 was apparently the first man to introduce the conception of absolute temperature in introductory lectures to chemists and he always considered himself as specializing in chemical physics. The orthodox chemists seem not to have taught this before 1880. The latter period of thermodynamics is also somewhat suspect, because it merges pretty completely with what I have called the fifth period.

As the fifth period I put the development of physical chemistry. Of course, Davy and Faraday are the real precursors of this period, but we usually consider it as starting with the discovery of the mass law by Guldberg and Waage. The names of van't Hoff, Arrhenius, Ostwald, Nernst, and Roozeboom are associated with the development of our knowledge in regard to osmotic pressure, electrolytic dissociation, the voltaic cell, and the phase rule. For the moment this development is in a bad way, apparently because the men, who for many years fought against the slightest modification of the electrolytic dissociation theory as at first put forward, have now gone to the other extreme, and have discarded the early concept of electrolytic dissociation completely. This confusion is not likely to last long and there are already signs of a return to sanity.

The sixth period, which is now in full swing, is that of atomistics, with Clerk Maxwell, Boltzmann, Rutherford, Moseley, Lewis, Langmuir, and Bohr as the chief protagonists.

The seventh period, and the one that we are interested in to-day, is that of colloid chemistry. The first colloid chemist of note was unquestionably Baudrimont in France, and the second

was Selmi in Italy, but neither of them has had any influence whatsoever on the development of the subject. Everybody agrees that colloid chemistry begins with Graham. The important subsequent names are Carey Lea—who, however, failed to make the impression he should have made—van Bemmelen, and Freundlich.

When one considers that Baudrimont knew more colloid chemistry than Graham twenty years before the latter, one wonders why Graham receives all the credit and Baudrimont none, not even from his fellow-countrymen. My guess is that Graham owed his success to his discovery of dialysis. In his hands colloid chemistry led to the discovery of separation by dialysis. Since a great many people used dialysis, they took with it the conception of colloids. As a matter of fact, dialysis was about all there was to colloid chemistry for a great many years. Baudrimont apparently did not come out with anything that was important to people and consequently his work was forgotten and might have stayed forgotten indefinitely if it had not been dug up by Mr. Bender, of the Douglas Pectin Corporation.

Carey Lea discovered colored and water-soluble silver, which excited a great deal of interest temporarily because of the unexpected nature of the phenomenon. Colored and water-soluble silver did not fit in at that time, either into physics or chemistry, and Carey Lea's work ceased to seem important. It was not forgotten entirely, partly because the time interval was too short and partly because of the bearing it had on the theory of photography.

As I have said many times, colloid chemistry may be defined, popularly, as the chemistry of bubbles, drops, grains, filaments, and films. This is neither a scientific nor an exclusive definition, because, for instance, a bubble is a film to the optimist who looks at the doughnut. It does emphasize the fact that a phase is called colloidal when it is sufficiently subdivided, or when at least one dimension of the phase is very small.

All colloidal phenomena involve or are accompanied by adsorption and in many cases the phenomena vary very much with the nature and extent of the electrical charge on the subdivided phase. Hardy was the first to consider the isoelectric point. Loeb's work is neither so new nor so important as he perhaps believed; but he did focus attention on the importance of the isoelectric point in a way that nobody had done before him. In

the case of colloidal solutions the Brownian movements are very important, the bombardment of the suspended grains or drops by the molecules of the liquid. In fact, adsorption and Brownian movements are the alpha and omega of colloidal solutions.

Colloidal solutions consist of particles small enough to be kept distributed through the liquid and prevented from agglomerating to larger particles by an absorbed film which either may act like a gelatine capsule or may be electrically charged and cause the particles to repel each other. Colloidal solutions are therefore stabilized directly or indirectly by adsorption of one or more of the other constituents of the solution. Both tannin and soap are apparently stabilized by adsorption of water. Silver chromate has been stabilized with sugar, silver bromide with potassium bromide. Gelatine is stabilized by electrolytes and water, while gold can be stabilized by a stabilized gelatine. Iron oxide can be stabilized by chromic oxide when this latter is stabilized or peptized by caustic soda.

When a colloidal solution is stabilized by an adsorbed ion, it will precipitate at the isoelectric point, and is usually fairly sensitive to the addition of electrolytes. On the other hand, tannin, which is stabilized by water, is extremely insensitive to electrolytes. Gelatine, which is apparently stabilized by the joint action of electrolytes and water, is relatively insensitive to the action of electrolytes, though it can be precipitated by sodium sulphate. The difference between colloidal gold, for instance, and gelatine with regard to the action of electrolytes is so striking that, in the early days, people distinguished between suspensoids and emulsoids. A suspensoid solution was a colloidal solution in which the dispersed phase was a solid and was easily coagulated irreversibly by small amounts of electrolytes, while an emulsoid solution was one in which the dispersed phase was liquid, was not coagulated readily by electrolytes, and the coagulation was reversible.

While this distinction was a good one when it was made, it is of no value now because we can get every gradation between the extremes. We can make a suspension of oil in water which is extremely sensitive to electrolytes and behaves in every respect like a suspensoid solution. Albumin is precipitated reversibly by salts of the alkali metals and irreversibly by the salts of the heavy metals. Chromic oxide is very sensitive to electrolytes in acid

solution and relatively insensitive in alkaline solution. Gelatine can act either as a precipitating agent or as a protecting colloid, depending on the concentration and other conditions. Tannin is certainly a solid and is scarcely precipitated at all by salts. With increasing knowledge, we have found the impossibility of drawing arbitrary distinctions. We now know that anything which will cut down the protective action of the adsorbed film will increase the tendency of the particles to agglomerate and precipitate. The adsorption is specific and consequently the effect of any added substance will vary with the nature and concentration of the colloidal solution to which it is added. We know now that alcohol will precipitate certain electrically charged sols at relatively low concentrations, though it used to be an article of dogma that non-electrolytes had no precipitating action unless added in sufficient quantity to change the thermodynamic environment, whatever that may mean.

An emulsion consists of drops of one liquid suspended in another liquid. If we call one liquid oil and the other water, merely to prevent saying A and B, and not because one liquid is oil and the other liquid water, we see at once that theoretically there can be two types of emulsions, one with drops of oil suspended in water and the other with drops of water suspended in oil. While we can make an emulsion with apparently pure oil in apparently pure water, the concentration does not exceed one part of oil in ten thousand of water, so these emulsions are not especially interesting. Any ordinary emulsion has a third substance in it, which acts as an emulsifying agent and which determines the type of the emulsion. There are many experiments purporting to show that the type of emulsion changes for a given emulsifying agent from the oil-in-water type, let us say, to the water-in-oil type when the ratio of oil to water exceeds some special value. So far as can be learned, all these experiments are wrong. The experimenters merely determined the points at which their methods of emulsification ceased to be effective and not the non-existent points at which there was a reversal of type. Any substance which passes into the interface between the two liquids and stays there can act as an emulsifying agent.

If the emulsifying agent passes wholly or chiefly from one liquid to the interface, the liquid from which it passes will be the external phase. If a colloid substance passes readily through the

interface, as in the case of arsenious sulphide with ether and water, it will be very ineffective as an emulsifying agent. It is therefore very surprising that methyl alcohol, which is miscible in all proportions with benzene and water, should be said to act as an emulsifying agent. There are also difficulties about oleic acid emulsifying benzene in water. It is popular at present to consider certain molecules as having one relatively blunt end and one relatively sharp end. If the sharp end goes into oil and the blunt end into water, the principles of the wedge make it evident that in this case we can only have an emulsion of oil in water because the wedges would not pack well otherwise. It is difficult to see how one can predict, on this basis, which is the blunt end of carbon black and why it should go into oil rather than into water.

We find experimentally that calcium soaps are peptized by oil and not by water and that sodium soaps are peptized by water and not by oil. Quite irrespective of whether these are polar compounds or have one blunt end, one would predict that sodium soaps would emulsify oil in water and that calcium soaps would emulsify water in oil, and this is what actually happens. It is also clear that if one mixes calcium and sodium soaps, there must theoretically be a ratio for which the tendency of the calcium soap to form a water-in-oil emulsion is exactly balanced by the tendency of the sodium soap to form an oil-in-water emulsion. At this point the emulsion is on the point of turning itself inside out, whichever way it is. This point has been realized and, curiously enough, the ratio of sodium to calcium for soaps with olive oil and water is approximately the same as that in sea-water.

Now, protoplasm consists of liquid materials which we may call oil, water which we may call water, and sodium and calcium and calcium salts together with proteins, etc., which we may call soaps. If we consider protoplasm to be in certain respects like an emulsion of oil and water with calcium and sodium soaps, it is a very mild further assumption to postulate that protoplasm is most active and healthy when it is near the point where the type of emulsion changes. If we make these postulates, we must draw the conclusion that calcium and sodium salts will have a mutually antagonistic action under certain conditions in presence of protoplasm, and this actually occurs.

Jacques Loeb showed that *Fundulus*, an organism found in San Francisco Bay, thrived in salt water but died eventually in

fresh water. This could be accounted for on the assumption of osmotic pressure, the fresh water flowing in and bursting the cells, thereby causing death, just as washing out the abdominal cavity of a human being with pure water instead of with a physiological saline solution is likely to cause hemorrhage and death. The difficulty with this hypothesis was that *Fundulus* died more quickly in an isotonic sodium chloride solution than in pure water, which could not be an effect of osmotic pressure at all. *Fundulus* also died quickly in an isotonic solution of calcium chloride, the next most important constituent of sea-water; but thrived fairly well in a solution containing sodium and calcium salts in approximately the ratio that they occur in sea-water without very much reference to the absolute concentration.

This state of things could not be accounted for by the physical chemistry of that day, because it involved an antagonistic action between sodium and calcium salts, either one alone being distinctly toxic to *Fundulus*, while a mixture was beneficial. Clowes pointed out that the antagonistic effect of sodium and calcium salts became just what one would expect if one could consider the protoplasm in *Fundulus* as analogous to an emulsion. Whether this is or is not the true explanation, this hypothesis by Clowes was a distinct step forward, because it gave us a new concept. One must not take this actual ratio of the sodium and calcium salts (about 50:1) too seriously. It undoubtedly fluctuates with different soaps, though this has not been shown. If the ratio for olive oil and water had come out somewhat different from that in sea-water, we might have explained this by saying that protoplasm was adapted to a prehistoric ocean in which the ratio of sodium to calcium was different from what it is to-day.

Clowes used this same hypothesis to account for the results of Osterhout, who had found that the specific conductance of a certain piece of sea-weed decreased on addition of calcium salts and increased on addition of sodium salts. Clowes showed that a change to a water-in-oil emulsion on addition of calcium salts would decrease the specific conductance because the water would be the discontinuous phase. Production of an oil-in-water emulsion by addition of sodium salts would increase the specific conductance because the aqueous solution, which conducts much the better, is then the continuous phase. By precipitating an emulsion in filter paper, Clowes was able to duplicate Osterhout's experi-

ments very successfully. This would seem to be a satisfactory proof of the accuracy of the hypothesis; but that is not the case.

The physiological literature is full of cases in which there is an antagonistic action of salts; but, in many cases, these seem to be osmotic pressure systems and not emulsion systems. An emulsion, as we ordinarily have it, consists of drops of one liquid separated from the other liquid by a film of a third substance. Since the two liquids or solutions are non-miscible under the conditions of the experiment, there is no tendency for either to flow into the other. There is no question of osmotic pressure and the question does not ordinarily arise as to the semi-permeability of the film. In an osmotic pressure system we have two solutions in the same solvent—the pure solvent being a limiting case—on either side of the diaphragm. What we call the solvent always tends to flow through the diaphragm in the direction which equalizes the concentrations, if we ignore the temporary phenomenon of anomalous osmosis; while one or more of dissolved substances cannot pass through the diaphragm if it is semi-permeable. The nature of the membrane determines the type of emulsion in the one case and the direction of flow in the other, but the emulsion systems and the osmotic pressure systems are fundamentally different, and if Osterhout's sea-weed proves to be an osmotic pressure system, the fact that Clowes could duplicate Osterhout's results has no significance whatsoever.

It seems to be pretty well established that a gelatinous precipitate is one in which the individual particles contain a large amount of adsorbed water or whatever the liquid may be. If these highly hydrous particles coalesce into chains, networks, or loose agglomerates, we get a jelly. It seems probable that we can get anything from a relatively coarse structure to what is practically a continuous fluid. Since Bechhold was not able to construct any ultra-filter which would behave as a semi-permeable membrane to any substance that everybody agrees is in true solution, it seems that we should consider the permeability of a semi-permeable membrane as due to solubility and not to holes. This may include solubility in the adsorbed water and does not mean that the copper ferrocyanide, for instance, necessarily forms a continuous liquid film.

In the early work on osmotic pressure it was assumed tacitly that a membrane, once formed, remained semi-permeable unless

ruptured mechanically. If we consider it as a colloidal film, that is not necessarily true. Any substance which tends to peptize the film will tend to make it permeable. Some of the apparently anomalous cases of osmotic phenomena can be accounted for in this way. Barlow found that alcohol makes a copper ferrocyanide membrane permeable to sugar; but he overlooked the fact that alcohol coagulates the membrane and therefore makes it permeable to everything. Czapek's experiments on the apparent permeability of some plant membranes when the surface tension of the solution dropped to about two-thirds its normal value, were really experiments on the point at which the membrane disintegrated, though he did not know this. Walden found that a copper ferrocyanide membrane was permeable to a large number of organic acids, even though it stopped the sodium salts of these same acids. It has since been found that dilute acetic acid coagulates this membrane, making it permeable to everything. Incidentally this eliminates Walden's chief argument against the copper ferrocyanide membrane being an ion sieve, so this question is still a legitimate subject for discussion. It is quite possible that the puzzling permeability of cell membranes after death may be due to increased acidity.

If we have a positively charged colloid like stannic oxide and a negatively charged colloid like gold, the two will tend to neutralize and to precipitate within certain limits. This phenomenon is absolutely general and does not lead to the formation of chemical compounds in definite and multiple proportions. If we must give these precipitates a name, they can be called adsorption complexes. It is not even safe to call them adsorption compounds. It is very difficult to get people to realize that these precipitates are not definite compounds. They find it difficult to believe that no definite aluminum silicates are formed by precipitation from aqueous solutions, that we do not get arsenites of iron and magnesium in this way, that the alumina-alizarine lakes are not definite compounds, and that purple of Cassius is not a definite compound of gold and stannic oxide.

One of the striking phenomena due to adsorption is the catalytic action of porous masses. It seems to be quite certain that we have oriented adsorption of a gas by a solid just as we have oriented adsorption of a liquid film by a mass of liquid. The adsorption involves the opening of either a normal bond or a

so-called contravalence, which means an activation of the molecule. Consequently, we get reactions taking place at adsorbing surfaces at very much greater velocities than is ordinarily the case. Thus hydrogen and oxygen can remain as a mixture at ordinary temperatures for years without any measurable reaction taking place; but they may combine almost explosively if brought in contact with clean platinum-black.

Langmuir has shown that in many cases the adsorption films at a plane surface do not exceed one molecule in thickness. It does not seem to follow, however, that the adsorbed films can never exceed one molecule in thickness at a plane surface. The implied reasoning seems to be that one molecule of gas does not hold fast to another molecule of the same gas under ordinary conditions; but that proves nothing as to what it might do under the extraordinary condition of being held firmly by a solid adsorbing agent. Crows do not ordinarily catch each other in their claws, but, it is stated, on apparently good authority, that if a crow is staked out on its back on the ground, it will seize hold of any other crow that comes near, making a layer two crows thick at that particular point.

Since the precipitation of a colloidal solution involves merely enough agglomeration for the force of gravity to overcome the Brownian movements, there is no reason that a further agglomeration may not take place after precipitation and we find experimentally that this is very apt to happen. Many precipitates change appreciably on standing. Silver chloride runs through the filter much less readily if not filtered until the next day. The sulphides all change on standing and so do the hydroxides. Freshly precipitated beryllium hydroxide requires less than one-twentieth the amount of caustic potash to carry it into apparent solution that is needed a few days later.

At higher temperatures this change is so much more marked that we give the name of sintering to it. Soot becomes sandy on long heating; magnesia becomes denser the higher it is heated short of the melting point. Clay sinters to bricks or pottery. The brown gold obtained in assaying sinters at a moderate temperature and tungsten sinters at 2400°–2500°. A porous chromic oxide sinters so much when heated that the mass may be raised to incandescence.

Just as we have agglomeration of a precipitate; we can also

effect the disintegration of it, a process which is usually peptization when it results in the formation of a colloidal solution. Loosely agglomerated masses can easily be peptized chemically as opposed to mechanically or electrically. Marked adsorption apparently always tends to cause peptization. We may have peptization by a liquid, as in the case of tannin and water, soap and water, or pyroxylin and amyl acetate. We may have peptization by a non-electrolyte as with the hydrous oxides of iron, etc., which can be peptized with sugar or glycerol. Since sugar will prevent the precipitation of calcium silicate, silver chromate, and silver chloride, it will undoubtedly peptize these same substances under favorable conditions.

If one ion of an electrolyte is adsorbed more than the other ion, the adsorbed ion will tend to peptize the material adsorbing it and will therefore tend to form a colloidal solution containing positively or negatively charged particles according to the nature of the adsorbed ion. Freshly precipitated silver halides are peptized by dilute silver nitrate or by the corresponding potassium halide, the silver and the halide ions being adsorbed strongly while the potassium and the nitrate ions are adsorbed but slightly. Silver bromide peptized by silver nitrate is charged positively and moves to the cathode during electrolysis. Silver bromide peptized by potassium bromide is charged negatively and moves to the anode under electrical stress. Zinc chloride peptizes zinc oxide forming what used to be called a basic salt in solution. Actually the zinc oxide does not form a definite chemical compound with zinc chloride and is not in solution. Most of the chlorides and nitrates of the heavy metals peptize their own oxides. Sulphides are peptized by hydrogen sulphide. Gelatine is liquefied or peptized by a potassium iodide solution. The peptization of the hydrous oxides of chromium, zinc, beryllium, cobalt, etc., by caustic alkali is due to preferential adsorption of hydroxyl ion. Hydrous chromic oxide gives an apparently clear green solution when treated with an excess of caustic potash and people used to say that potassium chromite was formed; but the green oxide is only in suspension and can be filtered out completely by means of a collodion ultra-filter, a colorless solution passing through. Hydrous beryllium oxide is peptized and not dissolved by caustic alkali and so is cobalt oxide. In ammoniacal copper solutions part of the copper oxide is apparently colloidal and part dissolved.

Freshly precipitated zinc hydroxide is peptized by alkali; but the solution is very instable, the zinc hydroxide often coagulating inside half an hour. The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate. The bulk of the evidence seems to be that alumina is not peptized appreciably by alkali and that it goes into true solution as sodium aluminate. Adsorption of hydroxyl ion accounts for the peptization of silicic acid and of casein by alkalies. Casein can also be peptized by acids, and colloidal solutions of aluminum, iron, cobalt, thorium, and yttrium oxides can be made by peptization with dilute hydrochloric acid. Ferrous oxide is apparently peptized by carbon dioxide and nobody seems to know whether the so-called calcium bicarbonate is in true solution or not.

The fairly stable and reversible colloids like gelatine, gum arabic, soap or saponin will peptize many precipitates, and they are often called protecting colloids because they prevent the agglomeration and consequent settling of finely divided precipitates. Casein is not peptized by water; but acts as a protecting colloid when peptized by acids or alkalies. When hydrous chromic oxide is peptized by caustic potash or soda, it can then prevent the precipitation of moderate amounts of hydrous ferric oxide. If too much ferric oxide is present, all the chromic oxide is carried down by it. Solutions of cupric oxide in ammonia will peptize chromic oxide, though ammonia itself will not.

While adsorption will cause peptization under suitable conditions, the disintegrating power of the adsorbed substance is relatively small and usually is not sufficient to break up solid masses. A protecting colloid, for instance, will prevent the formation of a precipitate when it may not be able to disintegrate a massive precipitate. For cases of this sort, we have to resort to mechanical or electrical disintegration.

If a solid be ground sufficiently fine, it will necessarily form a colloidal solution for a time. There is no difficulty in doing this with a brittle substance; but many substances coalesce again after they have reached a certain degree of fineness, so that one may even make certain fine powders coarser by attempting to grind them. The best way to get round this is to add some protecting colloid which will coat the particles as fast as formed and thus keep them from coalescing. It is possible to grind lead

in presence of glue and water. There is nothing new about this. The Chinese make their ink by grinding a special carbon black with a solution of gum and the Greeks used to grind gold leaf with honey. Some of the Lake Superior copper ores are said to be ground with oil to prevent smearing and the Acheson Graphite Company adds tannin when grinding its deflocculated graphite. Pitch may be ground with alkali-casein or rosin soap. One of the so-called colloid mills has a cone rotating very rapidly with just a thin film of liquid between it and the matrix. Apparently the water behaves like a plastic solid under these conditions and the solid particles are disintegrated by shearing.

When making solution, it is usually necessary to break up mechanically the liquid to be emulsified, as the emulsifying agent will not peptize it adequately. There are some curious things about this. When the constituents are mixed in a bottle and shaken in a shaking-machine, it is easy to make an emulsion of oil in water on a laboratory scale when the amount of oil is not too large. With a mechanical shaker giving four hundred shakes per minute and a 1 per cent. solution of sodium oleate, 80 per cent. by volume of benzene could be emulsified in water in fifteen minutes; but it took two hours to emulsify 96 per cent. of benzene, and 99 per cent. of benzene was not emulsified completely after eight hours of continuous shaking. If the shaking is done intermittently by hand, the number of shakes can be cut down enormously—from forty-eight thousand to eighty in the case of the 96 per cent. emulsion and from six thousand to seven in the case of the 80 per cent. one. Continuous shaking in a bottle disintegrates both benzene and soap solution into drops, the latter of which is disadvantageous. Since the soap solution is the continuous phase in these emulsions, any treatment which breaks up the soap solution retards emulsification. When benzene is dispersed into drops in the soap solution, the soap coats the drops and prevents them from coalescing, while there is nothing to prevent the rapid coalescing of the water drops in the benzene. The first few shakes cause the most disintegration of the benzene and the least disintegration of the soap solution, consequently intermittent shaking gives the best results.

For certain cases electrical disintegration is to be preferred to mechanical disintegration or to chemical peptization. When a

direct-current arc is formed under water between two wires, Bredig found that the metal was disintegrated and that colloidal solutions of platinum, iridium, palladium, gold, silver, and cadmium could be obtained in this way. A trace of alkali in the water causes formation of finer particles, presumably owing to the stabilizing effect of the hydroxyl ion. The disintegration is chiefly at the cathode. The method is not satisfactory with organic liquids, because there is too much decomposition of the liquids with formation of carbonaceous material. Svedberg found empirically that this decomposition could be decreased very much if the current density was made as small as possible. He used an oscillatory discharge from an induction coil with a condenser in parallel or in series. The best results were obtained with large capacity, small self-induction, low resistance, and short arc. By this improved method Svedberg succeeded in preparing colloidal solutions of all the metals, including the alkali metals. Liquid methane, ether, and isobutyl alcohol at low temperature were especially satisfactory with the metals of the alkalies and the alkaline earths. The most obvious explanation of the method is that the metal is volatilized and condensed; but this is not the whole truth, because Kutscheroff has examined the colloidal material under the microscope and finds that it consists of two portions: Globules, all about the same size, which are probably condensed from the vapor, and a colloidal powder which he considers as due to electrical bombardment. Richtmyer has found that, in making sputtered films from selenium, the deposit is amorphous or metallic if the selenium electrode is amorphous or metallic. If the deposit were condensed from vapor, it would be the same, regardless whether the starting solid was the amorphous or the metallic modification. Another reason for thinking that more than one factor comes in in the Svedberg process is that the order of disintegration of some of the metals under similar conditions was found to be Fe, Cu, Ag, Al, Ca, Pt, Au, Zn, Sn, Cd, Sb, Tl, Bi, Pb, the iron being the least rapidly disintegrated and the lead the most rapidly. There is no apparent relation either with the order of the boiling points or with the order of disintegration by cathode rays or canal rays.

Mention has been made that colloid chemistry is the chemistry of bubbles, drops, grains, filaments, and films, and it may perhaps

be well to show that these things are of technical importance and everyday interest.

BUBBLES.

One of the important technical uses of bubbles is in ore flotation. If we have, for instance, a sulphide ore in a siliceous gangue, the sulphide ore is wetted preferentially by certain oils, while the siliceous gangue is wetted preferentially by water. If we take an ore pulp containing one ton of ore to four or five tons of water, add twenty pounds or less of a suitable mixture of oils, and agitate the mass vigorously, we shall get a froth consisting of air bubbles coated with an oil film, the oil being stabilized and made viscous or plastic by the adsorbed particles of sulphide ore. We get thus a very stable, armor-plated froth which rises to the surface because the mean density of the air bubbles, oil, and sulphide particles is less than that of the water. The siliceous gangue settles to the bottom because it is wetted by water and does not stick well to the oiled bubbles. We have thus a very cheap method of concentrating ore, and millions of tons of lean ores are treated in this way every year. It is customary when talking about the process to say that the ore goes into the oil and the gangue into the water, which would imply a 100 per cent. separation. That is not to be taken too literally. Some gangue always goes into the oil and the percentage increases the finer the gangue. The ideal condition would be therefore to have the gangue particles coarse relatively to the ore particles; but one can hardly expect a mill to differentiate much between two sets of particles.

I don't know the total value of the bread baked in this country per year, but it must be very large, and it is quite possible that the value of the bread output exceeds the value of the ore obtained by flotation methods. If so, bread would be the leading bubble industry because bread without bubbles is quite uneatable, though perhaps not unthinkable. Some, and perhaps all, of the floating soaps owe their floating properties to the incorporation of bubbles in the mass. Unkind people have suggested that this was done at one time to decrease the amount of soap in the cake, and that the advertising value was an afterthought, but this is probably only partially true. What is known as "fluffed" ice-cream is said to owe its special characteristics to air bubbles. Fire-foam is a carbon dioxide froth made by mixing aluminum sulphate and

sodium bicarbonate solutions, to which a little licorice or other organic colloid has been added. Its function is to blanket the burning material and thus to prevent air getting to it. This is very effective with burning liquids, as in the case of oil tanks.

Carbonated drinks of one sort or another account for a great many bubbles. The difference in the relative permanence of the froth for beer and champagne, or for near-beer and ginger ale, is a question of the amount of colloidal material in the liquid. If this is high, the froth will be quite permanent and one may even get the phenomenon which used to be known as a collar.

White hair in animals is due to the presence of minute bubbles which scatter light, the diffuse reflection giving the sensation of whiteness. Curiously enough, human hair does not contain these bubbles so far as our experience goes; but owes its whiteness to differences in the material of the hair itself. There is no blue pigment in the feather of any bird. The blue color is due to innumerable minute bubbles in the horn of the feather which scatter blue light and to a black backing which keeps out all transmitted light. The blue feathers of the blue jay, the indigo bunting, the blue bird, and the kingfisher are typical instances.

DROPS.

The most important and the most widespread occurrence of drops is as clouds or fog when the drops are small and as rain when the drops become larger. The problem of fog dispersal or of making clouds rain is purely one of causing the very fine drops to coalesce into larger ones.

It has already been pointed out that emulsions are drops of one liquid suspended in another. Milk, cod-liver oil, and mayonnaise are typical emulsions and margarine is another. Lanolin is usually an emulsion of water in purified wool-fat, the emulsifying agent being probably isocholesterol. Some lubricating greases are made by emulsifying water in heavy oils by means of lime soaps. It is possible to keep the pigments suspended better in ready-mixed paints by emulsifying a little water in the linseed oil. Of course, this can be carried too far and a high admixture of water is unquestionably an adulteration. The rubber latex is usually considered to be an emulsion.

When making metallic sodium by the electrolysis of fused caustic soda, we find that there is an upper and a lower tempera-

ture limit. The lower temperature limit is of course approximately the temperature at which the bath freezes. The upper temperature limit is the temperature at which the losses become too great because of the peptization of the molten sodium by the bath and the resulting carrying of the drops of sodium to the anode by convection currents. With caustic soda the permissible temperature range is only about fifteen degrees; with aluminum it is said to be about seventy-five degrees.

In the manufacture of phosphorus and of zinc, the problem is to avoid the formation of drops. Both these elements are distilled, and if any air comes in contact with the condensing vapor, the material comes down as separate drops and does not coalesce to a liquid mass. With zinc the cold product is known as blue powder.

GRAINS.

When we heat clay, the grains may sinter to give us bricks or pottery. Porcelain is essentially a fused feldspar glass with grains of aluminum silicate in it. The ordinary white enamel is a glass made white by grains of stannic oxide, zirconia, calcium phosphate, or something similar, the grains having a different index of refraction from the rest of the glaze. Cement is a granular substance produced on a very large scale.

If we shake up a moderately coarse powder with a much finer powder, the finer powder does not first fill the voids in the space occupied by the coarser powder, as one would expect. It tends to coat the coarser powder. Fink has shown that a given mixture of a white, non-conducting powder like thoria with a black conducting powder like tungsten, will be black and conduct electricity if the tungsten powder is finer than the thoria powder and consequently coats the latter. The mixture will be white and will not conduct the electricity if the tungsten powder is coarser than the thoria powder and is consequently coated by the latter.

Briggs has shown that a deep blue powder is obtained if thirty-two milligrams of Prussian blue is mixed with ten grains of dolomite which passes a 40-mesh sieve and does not pass a 100-mesh sieve. In this case the Prussian blue particles coat the dolomite particles. If a mixture of the same percentage composition is made up, using ten grams of dolomite, all of which will pass a 200-mesh sieve, the powder is practically white. In another experiment 1 per cent. of ferric oxide colored the dolomite a

full red when the rouge passed a 200-mesh sieve and the dolomite did not pass a 100-mesh sieve. When the dolomite passed a 200-mesh sieve and the iron oxide did not pass a 100-mesh sieve, the powder was practically white. In a third set of experiments eight milligrams of lamp-black blackened ten grams of dolomite which was coarser than 40-mesh. When the dolomite was ground so that it all passed a 200-mesh sieve, six hundred and fifty-four milligrams of lamp-black, or over eighty times as much, was necessary to give approximately the same tint.

This behavior of powders is of great importance when using inert fillers in mixed paints. Many of the brands of para-red paints contain as high as 90 per cent. of ground barytes without affecting the color. Precipitated barium sulphate cannot be used, because it would mask the red color. The opacity of paper may be increased by grinding the filler more finely.

In phosphate baking powders, the monocalcium phosphate is protected from moisture by an admixture of starch, and it is well known in the trade—though at one time a valued secret—that the calcium phosphate must not be too fine nor the starch too coarse; potato-starch cannot be substituted for corn-starch. Cerebros salt, which is sold in England as a non-caking salt, contains an admixture of calcium phosphate which probably acts as a protecting film.

In photography the silver bromide grain is the unit and the properties of the plate depend on the quality of the grain. The hardening of steel and of duralumin is now believed to be due to the production of very fine grains throughout the mass of the metal. In making tungsten filaments for incandescent lamps, the grain size must be just right. The filament will sag if the crystals are too large.

The colors of colloidal gold and silver vary with the grain size. Carbon inks are suspensions of carbon particles in water. The luminosity of candle, oil, gas, and acetylene flames is due primarily to the presence of carbonaceous particles heated to high temperatures so that they are self-luminous. High temperature alone is not sufficient, for the non-luminous flame of a Bunsen burner is much hotter than the luminous flame. Ordinary smoke is carbonaceous matter suspended in air, and dust clouds contain solid grains of the local soil. The smoke screens used during the war consisted of fine particles of the oxides of phosphorus,

silicon, titanium, or zinc; or of particles of ammonium chloride. The so-called sneeze gases and some of the tear gases were really smokes, solid particles suspended in air.

To illustrate the theory of the structural color of blue feathers, Mason heated pieces of hard-glass Jena tubing in a combustion furnace at a temperature somewhat below the softening point of the glass, causing the production of minute crystals which scatter the light. Two hours of heating is usually sufficient; but the time can be shortened by raising the temperature. A strong, clear blue results, which changes to an opal white if the heating is prolonged unduly. By a suitable length of heating the partially devitrified Jena glass tubes can be made to give blues ranging from deep indigo to pale sky-blue or even white. The color may be brought out strikingly by painting the inside of the tube black, so as to cut off all transmitted light. The blues of such specimens are quite wonderful.

These blues and those of blue feathers are known as Tyndall blues and are due to the scattering of light by minute particles, which are solids in the case of the glass tubes and air bubbles in the case of the blue feathers. The blue of the sky is a Tyndall blue and is at least in part due to the scattering of light by fine particles. The blues of the early Chinese pottery were Tyndall blues and not dúe to pigments. This is the color which is said to be "as blue as the sky after rain when seen between clouds." The bluish bloom on some fruits and the blue of the blue spruce are Tyndall blues, being due to the scattering of light by fine hairs or fine powder. A more prosaic case of a Tyndall blue is the bluish color of cigarette smoke when viewed from the side and not by transmitted light. This blue disappears when the smoke particles get too large.

The gas masks used during the war owed most of their effectiveness to the granular charcoal which they contained. Perhaps the most important technical use of the properties of grains is in contact catalysis by means of pulverulent substances. Contact sulphuric acid is made by the combination of purified sulphur dioxide and oxygen at 425°–450° in presence of finely divided platinum. The platinum is often used in the form of platinized asbestos or of platinized magnesium sulphate. Other materials, like ferric oxide, will give similar results, but not at as low a temperature. The synthesis of ammonia from nitrogen and

hydrogen takes place in the Haber process at about 550° and 200 atms. pressure with iron or iron admixed with other things as catalyst. Claude has modified the process so as to work at a pressure of about one thousand atmospheres. The oxidation of ammonia to nitric oxide is done according to the Ostwald process with platinum as catalytic agent. Ostwald preferred to do this oxidation at about 300°; but American practice favors much higher temperatures, above 825°, for instance. The hydrogenation of oils has now become an important industry, with nickel as the usual catalytic agent.

FILAMENTS.

Under filaments we find the textile fibres, silk, wool, and cotton; the various types of rope; paper; hair and fur; artificial silk; leather, rubber and electric light filaments; asbestos; fibrous alumina, silver, potassium chloride, etc.; coke.

The textile fibres differ very much in physical and chemical properties. The silk fibre consists of a continuous thread which is spun by the ordinary or mulberry silkworm. The raw silk, as unreeled from the cocoon, consists of a double thread, 350–1200 metres in length, covered by, and cemented together with, silk gum or sericin. The smaller diameter of the single thread is about 13μ and the larger diameter about 26μ. Silk differs from wool and cotton in not having a cellular structure. The almost colorless fibre is very lustrous because of the smoothness of the surface and the fineness of the filament.

Wool is a modified form of hair and the term applies usually to the fleece from sheep, though some goat hairs are classed as wool. Wild sheep produce two kinds of hair, a long stiff fibre known as beard hairs, and a shorter, softer, and more curly fibre, which is the true wool. By domestication and proper breeding, sheep can be made to produce wool almost exclusively. Merino wool consists only of wool hairs; English Leicester wools consist only of beard hairs, while common, native wool consists both of beard and wool hairs. There is no sharp dividing line between wool and hair, and Barker says that one can find all gradations from the finest and softest merino to the rigid bristles of the wild boar. "Thus the fine soft wool of the merino merges into the cross-bred of New Zealand; the cross-bred of New Zealand merges into the long English and lustre wool, which in turn

merges into alpaca and mohair materials with clearly marked but undeveloped scale structure. Again, such animals as the camel and the Cashmere goat yield fibres which it would perhaps be difficult to class rigidly either as wool or as hair."

The outer layer of the wool fibre consists of horn tissue in the form of flattened scales which usually overlap and make the edge of the fibre serrated. It is this serrated edge which makes it possible to felt wool. Since neither silk nor cotton has these scales, it is a simple matter to identify wool under the microscope. On merino wool there are 110–120 scales per millimetre length of fibre. Wool is distinctly wavy, there being more waves to the inch and more regular ones the finer the wool. With the best merino wool, there may be thirty waves per inch. Wool is almost circular in cross-section, and the diameter varies from 10μ to 100μ.

Cotton is the seed hair of the cotton plant, which belongs to the mallow family. The cotton fibre consists of a single, long, tubular cell with one end attached directly to the surface of the seed. The long Sea Island cotton, grown on the islands off the coast of Georgia and Florida, has a fibre nearly two inches long, while the fibre of the short native cotton of India rarely exceeds three-quarters of an inch in length. The diameter is 15μ–40μ, the cotton with the longest fibre being usually the finest and consequently the silkiest. While growing, the fibre is round and cylindrical with a central canal running through it; but, after the enclosing pod has burst, the cell collapses, forming a flat, ribbon-like fibre twisted into the form of an irregular spiral or screw-like band, owing to the unequal collapse and contraction of the cell-wall on drying. The number of twists varies from 120 to 360 per inch, being greatest with Sea Island cotton. The twists are not a complete revolution of the fibre on its central axis, but are sometimes in one direction and then in the other. There are seldom more than five or six twists in one direction and often only one or two before a reverse twist takes place. The reason why the twists are never so numerous in the fully ripe fibres of coarse cotton is that these fibres are more rigid than the finer and longer staples, and therefore resist torsion better.

The colloid chemist is especially interested in these fibres because of their behavior with dyes, the adsorption being markedly selective. Speaking broadly, we may say that silk and wool absorb acid and basic dyes fairly strongly, whereas cotton does

not. With cotton, one must use a mordant, in general an acid mordant for basic dyes and a basic mordant for acid dyes. Substantive dyes dye cotton direct without the use of a mordant. Since the adsorption is selective, we are not surprised to find that cotton is dyed more strongly than wool by some substantive dyes and less strongly by others. With the so-called mordant dyes, a mordant is necessary with all three fibres, though wool and cotton are the ones that are usually considered.

The textile fibres are woven into cloth; but paper is made by beating fibres in presence of water until they become more or less gelatinous and then felting them together by letting them settle on some form of a sieve with continued shaking. Any fibre can be used which meets these requirements. The first paper was made by the Chinese from the inner bark of the paper mulberry tree. The Latin word for book, *liber*, literally meant bark. Flax and cotton were used later and, nowadays, most paper is made from wood-pulp in some form.

The carbon filaments, which were formerly used in incandescent lamps, were made by squirting a colloidal solution of cellulose in zinc chloride through small holes into alcohol, precipitating the cellulose which was afterward carbonized. Artificial silk is made by forcing a colloidal solution of cellulose or of cellulose nitrate through small orifices. In the Chardonnet process cellulose nitrate is peptized in an ether-alcohol solution and spun through fine glass jets into air or water, the threads thus obtained being twisted together to form the threads used in weaving. The pyroxylin threads are denitrated. In the cuproammonium process, the cellulose is peptized by an ammoniacal solution of copper oxide, which is in itself partly colloid, and is then run into a strongly acid bath which precipitates the cellulose. In the viscose process the cellulose is peptized by carbon bisulphide and alkali, and is precipitated either in an acid bath or in a concentrated solution of ammonium salts.

Leather is a fibrous material. Raw skins are readily putrescible when moist and are easily disintegrated by bacterial or chemical action. When dried, the collagen fibres glue together and the hide becomes hard and horny. In this state it will not putrefy; but it again becomes putrescible when brought in contact with water. When the hide is converted into leather by tanning, the tendency to putrefaction is overcome, the fibres do not

become glued together when the material is dried, but remain supple, and the material does not take up water appreciably when wetted. Vegetable tanning, which was practically the only form for many centuries, involves the adsorption of some form of tannin by the hide fibres, whence the name. Many people still believe that a definite compound is formed under these conditions; but this seems to be one of the beliefs that die hard. Comparatively recently, chrome tanning has become of great importance. The essential feature of this is the adsorption of chromic oxide or of a basic chromic sulphate by the collagen fibres.

When rubber is precipitated from the latex, the particles coalesce partially and form a fibrous mass. The methods of getting the rubber out of the latex are what one would expect in cracking an emulsion. The wild South American rubber is coagulated by evaporating; but the plantation rubber is precipitated with acid. Alcohol will also coagulate the latex, but is of course too expensive. One thing that bothers the people who would like to believe that all latices are alike, even though they are not, is that Castilloa latex can be precipitated quite satisfactorily by centrifuging, while this process does not work very well with Hevea latex, and fails completely with Lagos latex. Since the rubber globules in the Castilloa latex are about 3μ in diameter as against 2μ for Hevea latex, and less than 1μ for Lagos, the different behavior toward centrifuging is exactly what one might have expected.

It seems probable that the vulcanization of rubber is due to the adsorption of the sulphur compound which constitutes ebonite; but this has not yet been proved. Whitby points out that in no respect is rubber more obviously or typically colloidal in its behavior than toward liquids which cause it to swell or disintegrate. Rubber imbibes certain organic liquids and swells. With raw rubber, the imbibition generally proceeds so far, especially if the mass is stirred, that the swollen rubber changes to a colloidal solution. With vulcanized rubber there is less swelling—the amount decreasing with increasing degree of vulcanization—and the rubber does not go into colloidal solution. No hard and fast line can, however, be drawn between raw and vulcanized rubber with respect to the extent of swelling, because some samples of raw rubber do not form colloidal solutions readily.

Good coke has a somewhat spongy structure and could be

considered either under filaments or films. Bone says that the most essential qualities needed in a good blast-furnace coke, apart from low ash content, are a peculiar combination of strength and porosity, so that the fuel, whilst capable of withstanding the weight of the superincumbent materials in the furnace at a depth of some sixty-five or seventy feet below the stock line, shall nevertheless be sufficiently porous to be both easily penetrated by the ascending furnace gases, and rapidly consumed by the blast at the tuyere level.

Jellies and gelatinous precipitates are certainly fibrous in some cases. Weiser points out that studies on specific jellies have led some to conclude that all jellies are made up of a framework of amorphous threads and others that they are composed of crystalline threads; while still others fail to find any threads or filaments at all but observe an irregular grouping of particles. It is not unlikely that there are various arrangements of molecular aggregates in different jellies and, perhaps, in the same jelly. In all cases it seems probable that the particles are highly hydrous as a result of the adsorption, and that they are linked together, forming an irregular mesh or network, in the interstices of which liquid is entrained.

When discussing gelatinous precipitates Weiser says that "gelatinous crystals are apparently extremely fine needle-shaped masses, so thin that they lack rigidity and so flexible that they can be bent and twisted into various shapes and may move under the bombardment of the water molecules like the spiral bacteria present on the teeth. A cluster or network of such needle-shaped flexible crystals which adsorb water strongly would form a viscous or plastic mass which is usually known as a gelatinous precipitate. If the crystals are compact and rigid rather than thin and flexible, they would not form a gelatinous precipitate unless they united into threads or strings that would possess the flexibility and elasticity which characterize a thin needle crystal. Obviously the particles need not be crystalline and, as a rule, they probably are not. A gelatinous precipitate is apparently a network of extremely finely divided particles which have coalesced to form flexible filaments or chains and which adsorb water strongly, and so are highly hydrous. When the particles do not adsorb water particularly strongly and when the tendency to coalesce into filaments or threads is not great, a high concentration

of the finely divided particles is necessary as in the case of calcium carbonate and barium sulphate. It is probable that neither tendency is very marked in the case of gold, which accounts for the fact that no one has prepared a gold jelly."

Weiser apparently considers that a jelly consists of myriads of hydrous particles that have formed into a network which entrains liquids. McBain says that a bar of good toilet soap consists almost exclusively of extremely fine curd fibres. The parallel arrangement of curd fibres accounts for the "feather" of good household soap. The white opaque systems form a complete contrast to soap jellies. Under the ultra-microscope it can be seen that the formation of a soap curd is due to the separation from solution of microscopic or ultra-microscopic fibres, which may be of very great length and which have been shown to consist of neutral hydrated sodium soaps. Hydrated sodium soaps in their solid stable form consist of these curd fibres, whereas hydrated potassium soaps form true lamellar crystals, the fibrous forms being evanescent.

"According to recent X-ray work of Piper and Grindlay, the curd fibres of sodium palmitate are built up from molecules of soap laid parallel to each other and placed end to end so that sodium comes next to sodium and paraffin chain is end on to paraffin chain. There are thus sheets of double sodium atoms 4.4$\mu\mu$ apart, that is, just twice the length of the single molecule determined by Langmuir in his monomolecular films. Curd fibres are probably to be regarded as true crystals. It is important to note that anisotropic soap solutions give no such X-ray pictures; these are confined to crystals and curds."

McBain and Miss Laing make a distinction between a soap jelly and soap curds. The jelly is clear and elastic, containing the soap in colloidal solution. They have found some very curious things in regard to the true soap jelly or gel. "The conductivity of a soap solution is quantitatively unaffected when it sets to a clear, transparent, elastic gel. The same is true of its osmotic activity, as measured by lowering of vapor pressure, and of the concentration of sodium ions as measured by the sodium electrode. Indeed, the only difference between sol and gel appears to be the mechanical rigidity and elasticity of the latter. Neither shows any structure in the ultra-microscope. During electrolysis the relative movement of the constituents of the

solution is independent of whether it is a clear elastic jelly or a fluid sol.

"The identity of the significant properties of sol and gel proves that the same equilibria exist in each. The colloidal particles in sol and gel must be identical in kind and amount. The unchanged conductivity shows that the process of electrical conduction is unchanged in kind and degree. . . . Some micellar theory of gels is clearly indicated. In the case of soaps, the structure is probably filamentous."

FILMS.

Thin films play a very important part in our everyday life. We paint wood and iron to protect them and to make them look better. If the woodwork in buildings is not protected by paint, it will be injured by the action both of rain and of summer heat. In the presence of much moisture, especially in such a position that it cannot dry quickly when wetted, it will soon be destroyed by rot and mould. If iron is not painted, it will rust rapidly under the action of damp air. These disadvantages are obviated to a certain extent if the surface is covered with a layer of drying oil or of a paint made from a drying oil. The drying oils, of which linseed oil is the only representative on a large scale, and the boiled oils obtained from them, are rarely used alone in painting and decorating. Linseed oil is used, however, to some extent alone as a priming on iron and on wood when the natural color is to be kept. Usually, however, the linseed oil is mixed with some pigment which has the double purpose of strengthening the film and of giving a decorative effect. Paint is essentially a mixture of oil and pigment if we ignore the fillers, driers and thinners, which are also used. Addition of resin to oil gives a varnish, while the further addition of pigment gives a varnish paint or enamel.

Andès waxes quite enthusiastic on the subject of the utility of varnishing. "From a mere utilitarian point of view, articles, whether consisting of wood, metal, glass, stone, leather, paper, etc., are varnished because the impervious film or coating preserves them from wear and tear, the oxidizing action of air and moisture, and all those extraneous, disintegrating and corrosive influences included under the term 'weather,' noxious gases, etc., acid fumes, and, in special cases, even from the strong acids them-

selves; at the same time the uniform smoothness, transparency and brilliancy of the film are pleasant to the eye and the touch. Owing to the presence of antiseptic and toxic substances in the resins, oils, etc., which enter into the composition of certain varnishes, these, in addition to preserving the objects to which they are applied from ordinary wear and tear, also protect them from the ravages of insects, *e.g.*, wooden structures, from white ants in tropical climates. Even in Britain the parasites which infest the timber of town dwellings usually avoid varnished wood. The varnishing of floors is therefore a better remedy than periodical scrubbing with carbolic soap. . . .

"In addition to preservative action, varnishes have a decorative effect. The application of a coat of varnish to any porous surface, dressed and smoothed in an appropriate manner, enhances its appearance by imparting thereto a uniform, polished, glassy lustre. Should the object to which it is applied consist of previously dressed wood, it not only brings into bolder relief the more prominent features of the wood, by filling the pores thereof with a transparent medium, but by a light and shade contrast (produced by the harder and denser fibres as against the softer and less compact) it brings prominently into view all the characteristic modifications and ramifications of the woody fibre of different timbers included under the term 'grain.' The whole structure of the wood is, as it were, brought to the same level by actual contact with glassy surface."

The whole theory of adhesives depends in part upon the fact that the cementing material adheres strongly to the two surfaces and hardens there, forming a film, though the joint is stronger the thinner the actual film is. A good glue-joint in wood will easily stand a strain of six thousand pounds per square inch. People have claimed that too much pressure must not be used in gluing surfaced wood, because a so-called starved joint is formed if the glue is pressed out too completely from the joint. Bogue says, however, that as the layer of glue between the wood pieces is made vanishingly small, the strength of the joint will approach its maximum value. The bond between the two pieces of wood should consist only of the interlaced threads of glue passing from the pores in one piece to the pores in the other. It follows, therefore, that, provided the glue is properly applied, and in a condition such that a fair degree of penetration occurs, there can

be no such effect as a starving of the joint and no such thing as too much pressure, as far as the glue is concerned. The advantageous results realized by high pressure can be explained only upon the assumption that such pressures are necessary to squeeze out the maximum amount of excess glue in the joint, and to minimize any slight inequalities in the perfection of the surface.

Aluminum stands in the electrochemical series quite close to magnesium and fairly near to calcium and the alkali metals. One would therefore expect it to corrode rapidly under almost any conditions, but this is not what happens. The oxide or hydroxide film which is formed is adsorbed so strongly by the metal that it stops further corrosion. The only reason why an aluminum wire or an aluminum saucepan does not corrode is because the air and the liquids do not come in contact with the metal. If we amalgamate aluminum, the oxide coating does not adhere and the metal corrodes rapidly, giving us the so-called fibrous alumina. Nickel also becomes covered ordinarily with a strongly adsorbed film of oxide or hydroxide and consequently does not rust. In the case of iron the oxide is usually not coherent and consequently the metal goes on rusting. It is possible, however, under special conditions, to give iron a coating of the magnetic oxide which protects the metal fairly well.

We usually consider that the noble metals do not corrode in the air; but it is something of a question how many metals can qualify under this definition. We know that platinum-black is always oxidized in contact with air, which makes it probable that platinum foil has an oxide film on it. Under ordinary conditions most metals do rust or corrode; but, fortunately for us, a good many of them soon stop corroding because of the formation of a protecting film. Zinc corrodes superficially and everybody knows that a copper roof turns green and then undergoes very little further change. The corrosion problem is admittedly a question of the behavior of protecting films. Calorized iron is one solution of the problem, phosphatized iron is another, nickel-plating is a third, galvanized iron is a fourth, and painting is a fifth. Passive iron owes its properties to an instable oxide, presumably FeO_2 or FeO_3, stabilized by adsorption on metallic iron. If lead peroxide did not form a protecting film over the lead grid, the lead storage battery could not exist.

The colors of thin films are very interesting. If we have a

thin film with light reflected from the front and back surfaces, it may happen that the crest of certain waves reflected from one surface will coincide with the hollow of waves reflected from the other surface, in which case this particular color will disappear and the film will have the complementary color. The color depends on the thickness and the refractive index of the film. With increasing thickness of film the colors are: Black, white, yellow, red; violet, blue, green, yellow, red; purple, blue, green, yellow, red; green, red, greenish blue, red; pale greenish blue, pale red, etc. To get these colors in their full brilliance a dark background is essential, so as to cut off all transmitted light. Well-recognized cases of thin-film or interference colors occur in soap bubbles and in oil films on the streets. The iridescent colors on carborundum crystals are due to thin films of silica which can be removed with hydrofluoric acid.

The metallic or iridescent colors in feathers are due to thin films. There is no bright-colored pigment in the tail feathers of the peacock, the throat feathers of the humming bird, or the neck feathers of the pigeon. The only pigment is a dark one which serves as a background. The color originates in the barbules. In the case of the peacock, the cross-section of the barbule shows a central pith or core about two microns thick. Enveloping this core are three thin layers or laminæ, of equal and uniform thickness and seemingly in contact, and each about 0.4μ thick. These make the barbule act as a multiple thin film and consequently the color does not disappear completely when the feather is immersed in a liquid of the same index of refraction. In the case of the pigeon, there is only a single film.

These metallic colors can be duplicated very satisfactorily by putting a thin film of a colorless varnish over a dark pigeon's feather; but the result is more garish than a real feather, because the film spreads over the feather as a whole instead of over each individual barbule. The curvature of the barbules with the resultant complexity of the surface of the feather, results in a softening and blending of the garish colors noticed in plane, thin films, because of the different angles at which different parts of the curved surface are viewed. No one can deny that the colors of thin oil films on an asphalt pavement are garish.

When one reflects that the changes in color correspond to almost infinitesimal changes in the thickness of the laminæ, one

marvels at the way in which the pattern of the peacock's tail feathers is reproduced in different feathers and different birds through successive generations.

The iridescent colors of Roman glass are due to thin films. In the samples that we have examined, the scales that flake off are multiple films consisting of three laminæ. We do not know why this should be so. The temper colors on steel are due to thin films. In pearls we have alternate layers of calcium carbonate and an organic substance. The irregularities in the thin films modify the effect very much. The colors obtained when one fractures black ice and the colors of opals are interference colors.

Writing and printing involve the production of ink films of special shapes on paper. Calico printing involves the production of colored films, which may form patterns, on cloth. Dyeing is usually considered as really staining, because the color seems often to be uniform throughout the mass. It is an adsorption phenomenon, however, and can therefore be considered as the formation of a film. Whenever a mordant is used, we know that it is essentially the mordant and not the fibre which is dyed. In the case of dyes—organic and inorganic—which are precipitated in an insoluble form, one might consider these as grains; but then any film can be considered as made up of coalescing grains.

Dyes are usually classified as basic, acid, substantive (or direct), developed (or diazotized), mordant, vat, sulphur, miscellaneous, and inorganic (or mineral) dyes. The basic and acid dyes are always in true solutions under the conditions of use, though methylene blue, for instance, goes into colloidal solution in presence of an excess of alkali. So far as we now know, all the others exist only in colloidal solution with the exception of sodium alizarate. Basic dyes are salts of color bases which dye wool and silk but do not dye cotton satisfactorily without a mordant. Substantive dyes are salts of color acids which dye cotton direct (without a mordant); they may also dye wool and silk. Developed or diazotized colors are substantive colors which are formed on the fibre by diazotizing one member and coupling this with another. Mordant dyes do not dye wool, silk, or cotton direct, but require a basic mordant. The true color often does not appear until the adsorbed reduction product is oxidized. Sulphur dyes are reduced and peptized by sodium sulphide; they dye cotton direct. The miscellaneous dyes include aniline black and

the natural dyes. The chief inorganic dyes for textiles are Prussian blue, chrome yellow, iron buff, and manganese bistre. Ultramarine blue is used a great deal with paper.

Since the basic and acid dyes are electrolytes in true solution, the relative adsorption by the fibres of the different ions in the bath is of great importance. A basic dye will normally be taken up most strongly in an alkaline solution and least strongly in an acid solution. A strongly adsorbed cation decreases and a strongly adsorbed anion increases the amount of a basic dye taken up by the fibres. Things are just reversed with an acid dye, which is normally taken up most strongly in an acid solution and least strongly in a basic solution. A strongly adsorbed cation increases and a strongly adsorbed anion decreases the amount of an acid dye taken up by the fibres. A good illustration of this is to be found in the action of sodium sulphate as an "assistant." The readily adsorbed sulphate-ion increases the amount of a basic dye taken up and decreases the adsorption of an acid dye.

Since the substantive dyes are in colloidal solution, Briggs has shown that the important factor in determining the adsorption is the degree of stability of the sol. Anything which tends to precipitate the dye will increase the adsorption until the coagulation becomes so great that the dye begins to settle out even in the absence of the fibres. Addition of a precipitating agent in increasing amounts will therefore first increase and then decrease the amount of adsorption by the fibres. On the other hand, addition of a peptizing agent will decrease the amount of dye taken up by the fibre or will strip dye from the fibre. This is exactly what happens. The dye is forced on the fibre by acid or alkali, or by sodium chloride, sulphate and phosphate, the amount of adsorption passing through a maximum with increasing concentration of the electrolyte. Soap and gelatine decrease the adsorption because they peptize the dye.

The existence of films of some sort is assumed in the case of most living cells and is considered by some people to be essential to life. Jacobs says that "the majority, though not all, of the theories of cell permeability presuppose a plasma membrane of some sort, which exhibits a differential permeability, permitting some substances to enter the cell with ease (alcohol, ether); others with difficulty (most salts, sugars, etc.); and still others not at all (most colloids). Such a membrane was postulated by Pfeffer

to account for his osmotic results, and has been accepted as a matter of course by most subsequent workers. However, there have not been lacking those who have attempted to explain cell behavior in other ways. For example, Moore and his co-workers came to the conclusion, as the result of observations on blood corpuscles and on the behavior of various artificial membranes, that the distribution of salts inside and outside of cells could be explained better by an adsorption hypothesis than by the usual membrane theory. M. H. Fischer, also, in connection with his studies on œdema, has supported the view that the volume changes, which occur when living cells are placed in various solutions, are to be considered as cases of colloidal swelling, having nothing to do with semi-permeable membranes, the importance of which in such processes he denies."

Lillie states that "the presence of thin films with semi-permeable properties can be demonstrated readily in certain regions of the cells, *e.g.*, at the external surface (plasma membranes), or at the surfaces of cell structures, such as nuclei, vacuoles, spheres, or alveoli. The chief, physiologically important, property of these films is their semi-permeability, or resistance to the diffusion of dissolved substances. It is well known that the semi-permeability of the plasma membranes disappears on death; semi-permeability thus appears to be a special feature of the living state; in all dead or dying cells the membranes become permeable to substances to which formerly they were with difficulty permeable or impermeable. Conversely, all permeability-increasing substances are destructive to living protoplasm (cytolytic substances). There is also evidence that this increase of permeability at death affects not only the most exterior protoplasmic film or plasma membrane, but also the film structure in the cell interior. The coagulative changes in dying cells, the changes then occurring in the physical consistency and tensile strength, and the phenomena of death rigor are evidences of profound structural changes in the protoplasm. Apparently the intracellular partitions undergo increase of permeability or breakdown at death; this is indicated by the fact that many chemical reactions which are absent or inappreciable during life proceed rapidly in dead cells; examples are the oxidase reactions which cause browning in fruits, potatoes and leaves, the production of large quantities of acid (like lactic acid), and the hydrolysis of

proteins and glycogen in autolysis. All these reactions are promoted by cytolytic substances. The indications are that compounds, which are kept apart during life by barriers of some kind, become free to interact when the protoplasmic structure alters at death. Apparently the type of structure characteristic of living protoplasm is one by which free diffusion is prevented or restricted."

Films may play an important part in plasticity. A mass is plastic when it takes a finite force to give it a permanent deformation and when cracks, if any, accompanying the deformation are self-healing. One type of plastic material consists of solid particles with a liquid film over them. Putty is a case in point, being particles of calcium carbonate held together by oil. Wet sand is also plastic in the ordinary sense of the term. The clayworkers use the word in a special sense because they introduce the further restriction that the mass goes to dry sand on being heated and then falls to pieces. It would also exclude putty because the oil would carbonize and burn out when heated.

What the clayworkers mean, and do not say, is that the liquid film must be gelatinous and must cement the solid particles together when heated. This means that the solid particles in the clay must have a gelatinous surface film, which is either alumina-rich or silica-rich and which will take up water again after being dried in the sun. No known mixture of colloidal alumina and colloidal silica will do this. Consequently, there must be other constituents in the film. Jenks found that addition of small amounts of lithium chloride makes kaolin very plastic so far as drying at 110° was concerned. No burning experiments have yet been made.

This is not the way that nature makes clay plastic because the lithium chloride makes alumina and not silica plastic, and the lateritic clays, which are alumina-rich, are not plastic. It is probable that the ordinary plastic clays owe their plasticity to the combined action of humus and some salt.

Lubrication depends upon the maintenance of a thin film of oil or grease between the journal and the bearing. Bingham says that in the early use of lubrication, fixed oils and greases were depended upon almost exclusively. The fixed oils, that is the non-volatile oils of animal or vegetable origin, are expensive, may become gummy and rancid, which interferes with proper lubri-

cation and the acids may corrode the machines. These oils moreover often solidify partially when only cooled slightly. The range of viscosities obtainable is also restricted by the small number of oils available in any quantity. With the advent of the mineral oils, these troubles were all overcome, so the battle which was waged between the mineral and the fixed or fatty oils was short and apparently decisive. . . . . The theory predicted that so long as the viscosity was sufficient to produce the necessary pressure required to carry the load, it was of no moment what the chemical nature of the lubricant might be, provided only that the quantity of lubricant was ample. The practice has therefore been to use an oil which is much more viscous than is really necessary and to accept a loss in power in order to insure against any discontinuity in the oil film.

This conception of lubrication ignored the colloid chemistry part of the phenomenon, the adsorption of the oil by the metal. We now know, thanks to the work of Hardy, Langmuir, Harkins and Bingham, that the fixed oils are adsorbed so strongly by metals that they are not squeezed out easily from between two metallic surfaces.

These illustrations will give some idea of the importance of bubbles, drops, grains, filaments and films. The only other matter to consider is whether colloid chemistry is essentially an outgrowth theoretically of the period of atomistics or of the period of physical chemistry. Most people, I am sorry to say, consider it as a special branch of atomistics; but, so far as I am personally concerned, the theory of colloid chemistry is a necessary consequence of the phase rule. My line of attack has always been to ask myself what changes in equilibrium must occur when any dimension of a phase becomes very small. This seems to me the profitable way to approach the subject, both because it is the deductive method and because it eliminates the element of mystery which is so distressing; but it is admittedly not the popular one.

STATISTICS published by the National Automobile Chamber of Commerce, 361 Madison Avenue, New York City, indicate that there are over 50,000 automobile and truck dealers in the United States. Public garages number nearly 60,000; there are close to 68,000 service stations and repair shops, and over 64,000 automobile supply stores.—(*Machinery*, April, 1925, 639.)

INORGANIC CRYSTALS.*

BY

PROFESSOR WILLIAM LAWRENCE BRAGG, F.R.S.

Victoria University.

As a result of the X-ray analysis of crystal structure, it has been found that the structure of many inorganic salts is extremely simple, and that we cannot trace any evidence of an association of atoms into definite molecules such as the chemical formulæ of the substances would indicate. There may possibly be some bond in a structure such as sodium chloride, to take an instance, which associates each sodium atom with a corresponding chlorine atom, but X-ray analysis tells us that the effect of such a bond, if it exist, must be extremely small. To a high degree of approximation, each sodium atom can be regarded as equally related to six surrounding chlorine atoms, and each chlorine atom to six surrounding sodium atoms. In other salts, symmetrical relationships of a similar kind between the metal and acid radicals exist. This has lent support to the view that we may regard the forces which bind the inorganic crystal together as electrical attractions between oppositely charged ions, as has been suggested by J. J. Thomson, Stark, Kossel, Lewis, and Langmuir. There are other types of crystal where the grouping of the atoms into molecules is apparent. For instance, the chemistry of organic substances and the analysis of organic crystals agree in indicating that the atoms of an organic molecule are linked by bonds, with a definite spatial distribution over the surface of each atom, intimately related to its chemical valency. The organic molecule consisting of atoms linked rigidly together retains its identity when the substance crystallizes from another phase. On the other hand, in the inorganic salts which are under discussion here, the electrical attraction of the charged atom in ionic form would seem to be exerted over a number of surrounding ions; the number has no direct connection with the valency of the atom, but is determined by geometry, certain simple schemes of marshalling the ions being common to a large number of salts.

* Address delivered Wednesday, September 17, 1924, on the occasion of the celebration of the centenary of The Franklin Institute.

When the ions are drawn together to form the crystalline solid, we must suppose that, in addition to the electrostatic force of attraction, a repulsive force which limits their approximation comes into play. The simplicity of the resulting structures suggests that this repulsive force is directed from the centre of each ion. The ions are to be regarded as spherically symmetrical bodies, so that when two atoms approach, the work which has to be done against the forces of repulsion is a function of interatomic distance alone. The well-known work of Born, Landé, and

FIG. 1.

Sodium chloride, NaCl.

Madelung on the energy of the crystal lattice is based on this assumption, and their calculations are in quantitative agreement with measurements on the heats of formation and solution of the alkaline halides. This point of view is attractive because it makes it possible to calculate the physical properties of the crystal in terms of certain simpler atomic constants. The masses of the atoms are known, and the forces of attraction may be assumed to be those between charged ions. If some estimate can be made, even an approximate one, of the mutual potential energy of two atomic systems which come close together, or of the compressibility of the atom, we ought to be able to calculate the heats of

formation, elasticities, natural free periods, specific heats, and equilibrium configurations of inorganic salts.

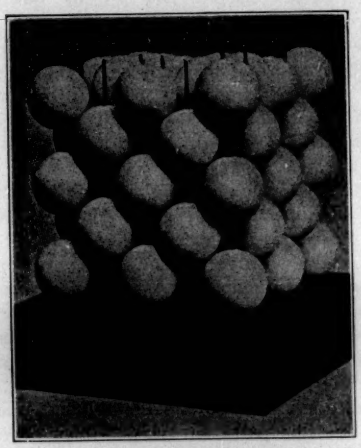
In the present paper some instances of the connection between properties and structure of inorganic salts will be described. We know as yet so little about the structure of the atom that this treatment of crystal-building can only be regarded as an approximation to be discarded later in the light of a more complete knowledge.

One of the most simple of all crystalline structures is that of sodium chloride, illustrated in Fig. 1. The atoms along any row parallel to a cubic axis are alternately sodium and chlorine, and consequently every positive sodium ion is surrounded by six negative chlorine ions, and *vice versa*. If we consider the atoms of one kind alone, such as the sodium atoms represented by the smaller spheres in the figure, it will be seen that they occupy the corners and face-centres of a cube. This arrangement is known as a cubic close-packed system, since a number of equal spheres will be packed together into as small a volume as possible if they are arranged in this particular way. There is an alternative method of packing the atoms equally closely which has hexagonal symmetry, and which is related to cubic close-packing. The two methods are shown in Fig. 2.[1] One may think of both systems as made up of layers of spheres, which are stacked one on another. In the cubic arrangement, these layers are perpendicular to the long diagonal of the cube, or trigonal axis; in the hexagonal arrangement they are perpendicular to the hexagonal axis. In a layer, the atoms are packed tightly together so that their centres outline a series of equilateral triangles. The next layer is laid on the first so that each sphere touches three below it. So far the arrangement is common to both cubic and hexagonal systems, but a difference is caused by the position of the third layer on top of the former two. If its spheres are directly on top of those of the first layer, an assemblage built on this scheme is hexagonal, but if the third layer is so placed that this is not the case, the assemblage is cubic. The structure is repeated every second layer in the one case and every third layer in the other. Both arrangements are equally tightly packed and the relative position of atoms in two succeeding layers is the same for both.

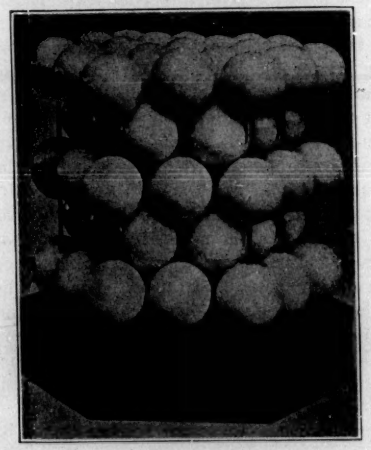
In sodium chloride, where the sodium atoms have the cubic

[1] These figures are taken from a paper by Pope and Barlow.

FIG. 2.



Cubic close-packing.



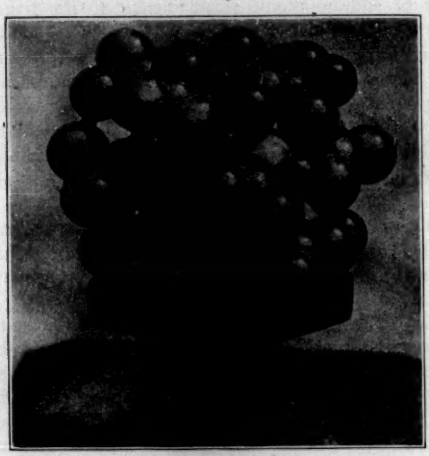
Hexagonal close-packing.

close-packed arrangement, a layer of chlorine atoms lies between each layer of sodium atoms perpendicular to the trigonal axis, a chlorine atom being in the space between three sodium atoms above it and three below. One could imagine a very similar pattern with hexagonal symmetry, in which the sodium atoms had the hexagonal close-packed arrangement. Since two succeeding layers of sodium atoms are the same in hexagonal and cubic close-packing, there would be exactly similar positions for the chlorine atoms in both cases, between three atoms above and three below.

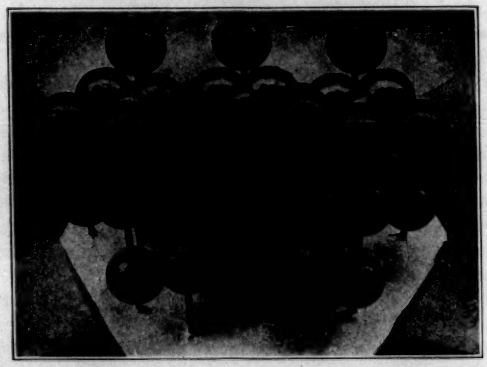
Actually, sodium chloride only crystallizes with a cubic structure, but there is a dimorphous compound, whose two forms have arrangements closely resembling the two alternatives depicted above. This substance is calcium carbonate, $CaCO_3$. In calcite the ions Ca^{++} and CO_3^{--} are arranged in the rock salt manner, whereas in aragonite they have the corresponding hexagonal arrangement. The CO_3 group consists of three oxygen atoms lying in a plane around a central carbon atom. Its oblate shape and lower symmetry, as compared with the chlorine ion, result in the calcite crystal being rhombohedral and not cubic, as if it were compressed along a trigonal axis. It is still true, however, that every calcium ion is surrounded symmetrically by six CO_3 ions, and *vice versa*. In aragonite, the calcium atoms have the positions of a hexagonal close-packed assemblage compressed along the hexagonal axis. The distances between atoms in the same layer, and between successive layers, is practically identical in calcite and aragonite, so that the two structures are very closely related. The CO_3 group fits into a space between six calcium atoms which have almost exactly the same configuration in both crystals. To a first approximation, the structures calcite and aragonite illustrate the two methods of arranging ions so that each ion of one sign has six neighbors of the opposite sign.

When we go into finer detail, X-ray analysis reveals a further difference between calcite and aragonite, shown by Fig. 3. The CO_3 group in calcite is so oriented that each oxygen atom is wedged between the calcium atoms, whereas in aragonite it has turned through 30°, so that the oxygen atom lies between three calcium atoms. This twist of the group is accompanied by a shift perpendicular to the plane of the diagram. In calcite the CO_3 group lies in a plane half-way between the upper and

FIG. 3.



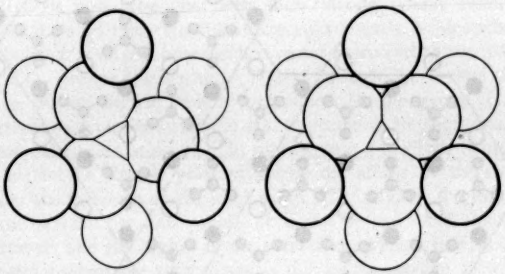
Calcite.



Aragonite.

lower calcium atoms, this being a necessary consequence of the symmetry of the structure. In aragonite the X-ray spectra show that it lies at one-third the distance between these same atoms. This particular position can be understood if the oxygen atom is so symmetrical that it takes up a position at the median point of the three calcium atoms between which it lies (Fig. 4). The centre of gravity of a triangle is at one-third the distance from the base to the apex, and as each oxygen atom fits into position between three calcium atoms, the whole group is in a position to enhance the third order X-ray spectrum of these planes, a feature

FIG. 4.



Calcite. Aragonite.

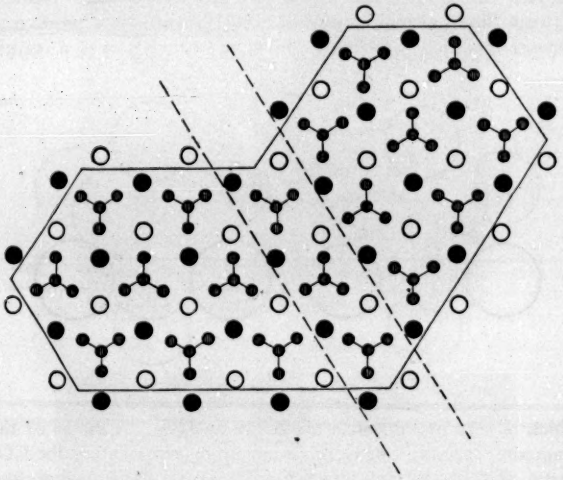
The situation of the CO_3 group in calcite and aragonite.

which is very prominent in the X-ray analysis. A model of the aragonite structure can be made simply by representing the CO_3 group as three spheres attached to a central carbon atom, and placing each oxygen in contact with three calcium atoms. Since the oxygen is equidistant from its three calcium neighbors, it seems to retain its spherical symmetry except at the point where it is attached to carbon. There is more room for the oxygen atom between three calcium atoms than between two, and we find correspondingly that aragonite is denser than calcite.

Although the structures of calcite and aragonite are complex, there is an underlying simplicity of marshalling the groups. The ions Ca^{++} and CO_3^{--} are arranged according to one of the most simple possible plans of alternations, so that every ion of one sign is surrounded by a number of the other sign. In this case the key-number is six. A very large number of crystals like

sodium chloride, and others where the acid radical is more complex, are based on the same scheme. When the acid radical is complex, the symmetry is generally of a lower type, and the exact details of the structure are more difficult to discover, but the simplicity of marshalling remains. Crystals have been analyzed when the key-number is eight (cæsium chloride) or four (zinc

FIG. 5.



blende), and these also are typical of classes of more complex substances.

The manner of arranging the calcium atoms in aragonite gives a structure with hexagonal symmetry. Actually, the crystal belongs to the orthorhombic system, although its axial ratios and optical properties are so nearly those of a hexagonal crystal that it is termed "pseudo-hexagonal." The reason for this is clear when the CO_3 groups are placed in position. One-half of the groups in a sheet between two planes of calcium atoms must face one way, and one-half the other, for reasons of symmetry. Fig. 5 shows a diagram of such a sheet; it is necessary to place the CO_3 groups in rows, so that all those in a row point the same way,

while alternate rows point opposite ways. This selects one of the pseudo-hexagonal axes, parallel to the rows, as different from the other two, and this is the unique *a* axis of the real orthorhombic structure. Aragonite very frequently twins, so that two crystals with common *c* axes have their *a* axes inclined at nearly 60°. In Fig. 5, two individuals are shown twinned together, and it will be noticed that a section of the crystal outlined in the diagram can be regarded as belonging to either individual. This perhaps explains the ease with which the crystal twins, since the relationship between nearest neighbors in the crystal is at no point altered by the twinning.

Calcite and aragonite both show strong double refraction. The nature of this refraction may conveniently be described by saying that a wave whose electric vector is parallel to the plane of the CO_3 groups travels more slowly through the crystal than a wave whose electric vector is inclined to the group (in the extreme case perpendicular to it). According to electromagnetic theory, the retardation of light passing into a medium from space is due to the electric polarization of the atoms of the medium under the influence of the light wave. The greater the total electrical moment per unit volume produced by the wave, the slower it travels and the higher is the refractive index. In $CaCO_3$ the greater part of the refractivity is due to the oxygen atoms, and the double refraction must be explained by the constitution of the CO_3 group. At first sight it appears difficult to investigate the behavior of such a group under the influence of a light wave. Three oxygen atoms are bound to a central carbon and the structure of all four atoms must be profoundly modified by the chemical bonds. The author has attempted to treat the problem by supposing that the oxygens, following Kossel, are symmetrical negative ions attracted to a central positive carbon ion. When polarized by an electric field, the oxygen atoms influence each other, and it can easily be shown that they aid each other's polarization when the electric vector is in their plane, while they tend to depolarize each other when it is perpendicular to their plane. Since X-ray analysis gives the distance apart of the oxygen atoms, and atomic refractivity gives their doublet strength for a given field, it is a simple matter to calculate their effect on each other. The interesting result appears that *the birefringence of calcite and aragonite is explained quantitatively to a high degree of accuracy by the rela-*

tive position of the oxygen atoms in the CO_3 group, without its being necessary to assume that the atoms themselves are anisotropic, reacting differently to local electric fields with different orientation. When the electric field of the light wave polarizes the oxygen atom, its position and negative parts are relatively displaced. A field is set up round it which is supposed to be equivalent to that of an electric doublet placed at its centre. The effect on each other of three such doublets, for different directions of the electric field, exactly explains the difference between the ordinary and extraordinary refractive indices 1.66 and 1.49 of calcite, and the corresponding indices of aragonite. This result is surprisingly simple, and must, of course, be tested by an examination of other crystals before we can be sure that the agreement is not accidental in the case of calcite and aragonite. The most loosely held electrons will be those most easily displaced by the electric field, and those electrons should be greatly influenced by the neighborhood of the carbon atom. In spite of this, the oxygen atom acts as if it were symmetrical in its response to the light wave. As yet very few doubly-refracting crystals, to which the same principles could be applied, have been analyzed by means of X-rays, on account of their complexity. The author has shown that the structure of Al_2O_3, aluminum oxide, explains the very small birefringence of the crystal, but no other material for test is available.

It will be very interesting to see whether the rotation of the plane of polarization by inorganic salts can be calculated in the same way by the relative positions of the atoms. The structures of sodium chlorate and bromate furnish suitable material, and an attack on this problem in a simplified form has been made by Hermann.[2]

The acid radicals CO_3^{--} and NO_3^{-} consist of three oxygen atoms lying closely together in a plane. When a crystal is composed of such groups oriented parallel to each other, analysis shows that the crystal must be optically negative. If the oxygen atoms in a group such as SO_4 are arranged in a tetrahedral manner, such a group should be optically isotropic considered by itself, on account of its symmetry. In this we may perhaps trace the reason for the small birefringence of most sulphates.

The marshalling of the ions is the same for NaCl and $CaCO_3$ (calcite), but the latter crystal is distorted from the cubic to the

[2] *Zeit. f. Physik.,* xvi, 1923, pp. 103–134.

rhombohedral form because the CO_3 ion is less symmetrical than the chlorine ion. The edges of a calcite rhomb meet at angles of 101° 55′ instead of 90° as in the cube. A number of carbonates have the calcite structure, and show a regular gradation of rhombohedral angle. For magnesium carbonate, the angle is 103° 22′, and it decreases fairly steadily with increase of molecular volume through zinc, iron, manganese, and cadmium carbonates to the calcite value. $CaCO_3$ appears to be in a critical position in the series, for the carbonates of strontium, lead and barium with still larger molecular volumes are of the aragonite type. In sodium nitrate, which has a structure like calcite, the rhombohedral angle is 102° 42′. Professor Chapman and the author have attempted to calculate the angle which is characteristic of all these crystals. The crystal of calcite may be regarded as a mechanical system under equilibrium between the stresses due to interatomic forces. If such a system be slightly distorted in any way, mechanical principles assert that the virtual work done by the various forces vanishes. The forces are taken to be electrostatic attractions between oppositely charged ions and repulsion due to the close approximation of neighboring atoms. If the crystal is so distorted that the distance between oxygen and carbon atoms and oxygen and calcium atoms remains constant, no work is done by the forces of repulsion. It is possible to calculate the work done by the electrostatic forces and see whether the potential due to them is actually a minimum at an angle of about 102°.

The mathematical calculation has been made by Professor Chapman, and we find that it assigns an angle to calcite which is about 4° too large. Considering the arbitrary nature of the assumptions that have been made, the agreement is interesting, though far from satisfactory. It is more encouraging to find that although the absolute value of angles are all too high, the alteration in rhombohedral angle when passing from one carbonate to the next by the substitution of a different metal is exactly explained.

Crystal structure will only receive a satisfactory explanation when we have full knowledge of the structure of the atom. In the meantime, there appear to be certain simple assumptions which can be made about the atom in the inorganic crystal and which enable us to link up its structure and properties to a certain extent. If each atom can be thought of as an ion with a sym-

metrical field of repulsion and electrostatic field of attraction, many of the properties can be understood. The intimate structure of the atom is not involved in the inorganic salts, whereas in the organic molecule, the binding force must be one of its manifestations. For this reason, the inorganic crystals promise for the physicist and physical chemist a fascinating field of research which we can explore with some hope of immediate results.

The Lustre Produced in Cotton by Mercerization. T. BARRATT. (*Trans. Faraday Soc.*, Dec., 1924.)—"It would appear almost obvious that the brilliancy of a mercerized fabric must be due to the swelling up of the separate fibres, and the consequent more or less cylindrical shape that they assume. This would give a smooth surface in place of the well-known twisted, irregular shape of the unmercerized fibre, and the result would be a more regular reflection of the incident light." With this simple explanation Huebner and Pope are not in agreement for they "attribute the lustre to the reflection of the light from spiral ridges still remaining on the surface of the fibres after mercerization." It is not so much with the physical basis of the changes caused by mercerization as with the measurement of the optical difference produced by the treatment with sodium hydroxide that this paper concerns itself.

A ray of light fell upon a surface consisting of fibres and after reflection, regular or irregular, proceeded to a photometer. Its entire path lay in a horizontal plane. The surface was covered in one case with glass fibres, again with mercerized fibres and in a third instance with fibres of unmercerized cotton. The angle of incidence was made equal to the angle of reflection so that reflection was regular. When the length of the fibres was horizontal the glass reflected 21.5 per cent., the mercerized cotton 20 per cent. and the unmercerized 18 per cent. of the incident light. With the fibres vertical the corresponding values have fallen to 13.7 per cent. and to 16 per cent. for both kinds of cotton.

Regular reflection was now discarded and, the fibres being horizontal, the angle made by the incident light with the surface was varied. The value of the observations thus made is impaired by lack of specifications of the direction in which the diffused light left the surface. The author claims that his experiments "bring out very clearly the fact that the light reflected from a mercerized fibre in certain positions is concentrated within a small angle. In the case of unmercerized twisted fibre the reflected light is scattered or spread out in a wider angle. A careful examination of a well-mercerized cotton fabric will show a distribution of very bright and very dull points, the total amount of reflected light being usually rather less than from the more uniformly lighted surface of an unmercerized fabric." G. F. S.

CONCENTRATION AND POLARIZATION AT THE CATHODE DURING ELECTROLYSIS OF SOLUTIONS OF COPPER SALTS.*

BY

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Member of the Institute.

IN A circuit consisting of storage battery, rheostat, ammeter, and cell (two copper electrodes in a solution of a copper salt), the potential difference between the electrodes may be measured while the current is flowing. With this arrangement, one or two milliamperes of the current measured by the ammeter may pass through the oscillograph element used as voltmeter—a serious matter with the small currents used in previous work;[1] but as in our experiments, currents of the order of one thousand milliamperes were employed, this small diversion caused no difficulty.

The potential difference observed is due in part to the $i.r$ drop through the cell, the remainder receives the name, "polarization." The polarization in turn is partly due to the difference in concentration at the two electrodes brought about by the electrolysis—"concentration voltage"; the remainder, so long as only copper is deposited at the cathode, is the "overvoltage." Thus:

$$P.D. = \overbrace{i.r \text{ drop} + \text{conc. voltage} + \text{overvoltage}}^{\text{polarization}}$$

and to determine the overvoltage, both (i) $i.r$ drop, and (ii) conc. voltage must be determined and subtracted from the potential difference given by the oscillograph. (i) The $i.r$ drop is given by the instantaneous fall in potential difference that occurs when the electrolysing current is stopped,[2] in our experiments it proved equal to the product of the current into the resistance of the leads, electrodes, and electrolytes; thus there was no "transport resistance" and no non-conducting film on the elec-

* Address delivered Wednesday, September 17, 1924, on the occasion of the celebration of the founding of The Franklin Institute.

[1] LE BLANC: *Abhandlungen d. deut. Bunsen-Ges.*, Nr. 3 (1910).

[2] This method of distinguishing between polarization and ohmic resistance was used by Le Blanc, *loc. cit.*, p. 58.

trodes. (ii) Le Blanc was one of the first to measure overvoltage with the oscillograph. He did not attempt to calculate the concentration voltages, but eliminated them as far as possible by cutting down the duration of his electrolyses. The concentrations at the electrodes, however, can be calculated from the current by Faraday's law and Fick's law of diffusion, as shown by Weber [3] in 1879. His differential equation was solved for certain simple cases and verified experimentally by himself, Warburg,[4] and Sand;[5] Professor Rosebrugh [6] and I developed the equations for the general case, and from these equations, if the current at each instant of the electrolysis be known, the concentration at either electrode at each instant may be computed from the limiting current and the diffusion constant of copper in the electrolyte.

APPARATUS.

The electrolytic cell consisted of a stationary electrode (*viz.*, a copper pot) and a rotating copper electrode of 92.5 sq. cm. surface. The pot was immersed in the water of a thermostat, and could be closed air-tight; all electrolyses were carried out with air-free solutions in an atmosphere of nitrogen or carbon dioxide. In order to secure uniform current-density and uniform liquid friction over the whole surface of the rotating (cylindrical) electrode, it was mounted on a vertical shaft between two others of the same dimensions. Each of the three was provided with its own rheostat, and during electrolysis each was supplied with the same number of amperes; but only the central electrode was used for determining the potential difference. While the currents were being set, the cell was out of the circuit, being replaced by equivalent resistances; automatic devices threw the cell into circuit a few hundredths of a second after the oscillograph shutter opened.

The potential difference between the electrodes was recorded by one of the two elements of a Siemens-Blondel oscillograph, while the time scale was provided by the other which was actuated by a current induced in the secondary of a small induction coil by the vibrations of a tuning fork (middle C, 128 cycles per second). On its way from the coil to the element, this current was carried

[3] WEBER: *Wied. Ann.*, 7, 536 (1879).
[4] WARBURG: *Wied. Ann.*, 67, 493 (1899).
[5] SAND: *Phil. Mag.* (6), 1, 45 (1901); *Zeit. Phys. Chem.*, 35, 641 (1900).
[6] ROSEBRUGH and LASH MILLER: *Jour. Phys. Chem.*, 14, 816 (1910).

past the axle of the rotating electrode and was short-circuited once for every revolution of the shaft, thus the speed of rotation of the electrode was recorded on the film.

The experimental work falls under two heads:

(I) Measurements to check the predictions of the diffusion theory: (*A*) Limiting-current measurements, (*B*) time measurements.

(II) Measurements of overvoltage, the concentrations given by the diffusion theory are accepted as correct and used to calculate the concentration voltages.

(I) MEASUREMENTS TO CHECK THE PREDICTIONS OF THE DIFFUSION THEORY.

(*A*) The "limiting current" is the minimum current that under the given experimental conditions can liberate hydrogen at the cathode, *i.e.*, that can bring the concentration of copper in the electrolyte at the cathode practically to zero. According to the diffusion theory (which assumes that the diffusion constant of the copper is independent of its concentration in the electrolyte), the limiting current should be proportional to the concentration of copper in the body of the solution (constancy of temperature and rate of rotation of the electrode assumed). The results of some hundreds of experiments show that this prediction is fulfilled, and lead to the empirical relation

$$I' = 107.4\, z_0 R^{0.77}$$

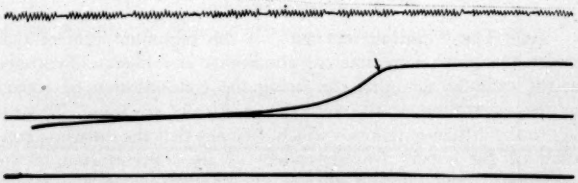
by means of which the limiting current (I' amperes, 92.5 sq. cm. cathode area) can be computed from the copper concentration (z_0, number of E.C.E. copper per c.c. of solution) and the rate of revolution of the cathode (R, number of revolutions per second), for electrolyses at 18° C. with solutions of copper sulphate in maximum-conducting (*i.e.*, 7.6 normal) sulphuric acid. Similar expressions were obtained for other experimental conditions.

(*B*) Fig. 1 shows a typical oscillogram obtained during electrolysis with a known constant current greater than the limiting current. The wavy line at the top of the figure is the record of the tuning-fork current; it gives the time scale for the abscissas and the rate of rotation of the cathode. The other two horizontal lines furnish the voltage scale for the ordinates; the lower of the two was traced with no potential difference over the element,

and the upper with a potential difference of 0.538 volt. The height of the curve above the lower horizontal line gives the potential difference between the electrodes at every moment of the electrolysis; the point marked by an arrow, where the curve shows a point of inflection, is taken to be the point at which the copper concentration at the cathode reaches zero.

From every such record of the time required to bring the copper concentration at the cathode from its known initial value to zero, a value of the diffusion constant of copper can be computed. Fig. 2 shows that 56 oscillograms obtained by electrolysing

FIG. 1.



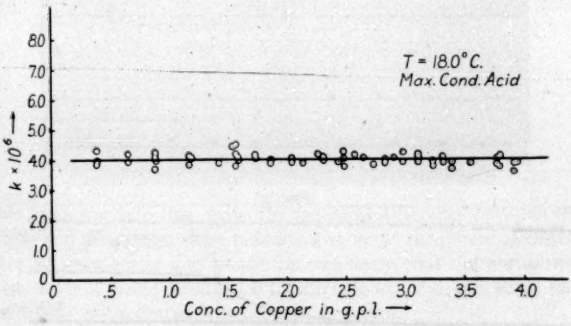
with different currents at 18° C. (solutions of copper sulphate in max. cond. sulphuric acid containing from 0.5 to 4.0 g. of copper per litre) give values of k grouped round 4.0×10^{-6}. The effect of temperature, and of the composition of the solution, on the diffusion constant were determined.

With the value of the diffusion constant known, as well as the expression connecting the limiting current with the copper concentration and the speed of rotation of the cathode, the equations derived from the diffusion theory enable one to predict the time required to liberate hydrogen when the intensity of the current, or its direction, or both, vary in any known manner during electrolysis. Fig. 3, for instance, is an oscillogram obtained during the electrolysis at 18° C. of a solution containing 1.425 grams of copper per litre of maximum sulphuric acid, with a current of 2.05 amperes (cathode area, 92.5 sq. cm.) which was periodically interrupted during the electrolysis; the duration of each beat of current and of each interruption can be read on the oscillogram, as can the rate of revolution of the cathode. The equations predict liberation of hydrogen 0.580 second after the beginning of the electrolysis; measurement of the oscillogram

gives 0.578 ± 0.004 second. In over one hundred such electrolyses—some with interrupted current, some with the rotating electrode alternately cathode and anode, some with a succession of four arbitrarily fixed currents, and some with combinations of direct and sinusoidal currents—the times necessary to bring the cathodic copper concentration to zero agreed within 0.01 second with those predicted by the equations.

In addition to these computations of individual cases, certain

FIG. 2.



general propositions which follow from the theory were experimentally confirmed, for example, the proposition that, with currents more than twice the limiting current, the rate of rotation should have no effect on the time required, and *vice versa*. Finally, a number of electrolyses have been carried out between stationary copper plates; the results in every case were in agreement with the predictions of the theory.

(II) MEASUREMENTS OF THE OVERVOLTAGE.

The diffusion theory, having thus proved its reliability, was then used to calculate the rapidly changing concentrations of the copper at the electrodes during the electrolyses. From the concentrations so computed, the concentration-voltages were calculated by the formula:

$$\text{Conc. vltg.} = 0.03 \log. z_0/z$$

where z is the concentration at the cathode and z_0 at the anode and *log* is the common logarithm. (This formula follows from

the theory of dilute solutions, for 18° C., on the assumption that in these acid solutions the copper sulphate is totally undissociated; it was moreover confirmed by direct measurements with the potentiometer.)

The results of such a calculation are shown in Fig. 4. In this figure, the oscillogram is that of Fig. 1, to which two lines have been added, *viz.*, a horizontal whose height above the zero

FIG. 3.

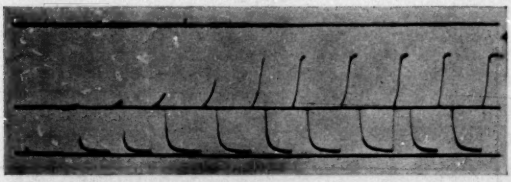
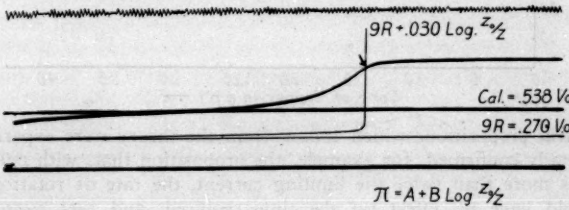


FIG. 4.



voltage line gives the $i.r$ drop, and a curve whose height above the $i.r$ line gives the concentration voltage. Thus the distance between the new curve and the curve drawn by the oscillograph gives the overvoltage up to the moment at which hydrogen is first liberated. The part of the new curve that projects above the oscillograph curve has no physical significance.

The percentage change of concentration at the anode, as computed from the equations, was trifling in comparison with that at the cathode, so that, in the expression for the concentration voltage, z_a may be replaced by z_0; moreover, measurements with auxiliary electrodes (copper gauze in the electrolytic cell, or reversible electrodes outside the cell communicating with the

electrolyte by siphons) showed that, under the conditions of our experiments, the overvoltage is almost exclusively cathodic. In obtaining the oscillogram of Fig. 5, for instance, both elements of the oscillograph were used to measure voltage; the heavy line is the common zero voltage line, the calibration line corresponds to 0.538 volt, the curve gives the potential difference between the cathode and a piece of copper gauze suspended in the electrolyte near the cathode, and the lower horizontal line, barely distinguish-

FIG. 5.

able from the zero line, gives the potential difference between the gauze and the anode. The numerical value of the potential difference between gauze and anode, its constancy, and the abruptness with which it disappeared when the current was shut off, show that there was no appreciable anodic polarization.

Mr. A. R. Gordon has found an empirical formula for the (cathodic) polarization, *viz.*,

$$\text{Polarization} = A + B.\log(z_0/z)$$

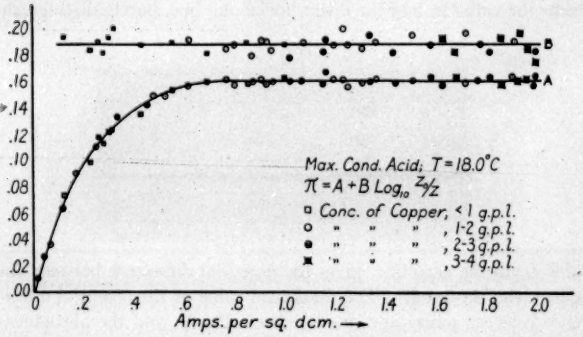
where z_0 is the copper concentration in the body of the electrolyte, and z that at the cathode. For the electrolysis recorded in Figs. 1 and 4, $A = 0.16$ and $B = 0.19$. This formula fits all the oscillograms obtained with constant current, from the beginning of the electrolysis to about the middle of the steep rise of the potential-difference curve; so that, for this range, at 18° C.,

$$P.D. = \underset{\text{conc.}}{i.r} + \underset{\text{voltage}}{0.03\ \log\ (z_0/z)} + \underset{\text{overvoltage}}{A + (B - 0.03)\ .\log\ (z_0/z)}$$

Fig. 6 shows that the value of B is independent of the concentration of copper (40 expts., 0.5 to 4.0 g. Cu per litre), and of the current-density (0.1 to 2.0 amp. per sq. dm., 40 expts.). It is also independent of the amount of sulphuric acid in the solution (4 expts., 0.5 to 7.6 normal), while A is independent of

the concentration of copper (52 expts.), but depends on current-density and acidity. With low current-densities, A falls to zero; in 7.5 N sulphuric acid, it reaches its maximum with 0.7 amp. per sq. dm. and retains this value for higher currents. For solutions of copper sulphate in 0.5 normal sulphuric acid the maximum value of A is 0.06, while in 7.6 N acid it is 0.16. Both

FIG. 6.



A and B decrease with rise in temperature, about 1 or 2 per cent. per degree (7° C. to 30° C.).

These results apply only to electrolysis with constant currents. Oscillograms obtained with currents whose direction was abruptly changed, so that the rotating electrode was alternately anode and cathode, gave a lower value of A than that observed with constant or interrupted currents. The "initial overvoltage" thus depends on the previous history of the cathode, and must be referred to some property of the cathode itself, as Reichinstein[7] contended, and not to some reaction in the solution (*e.g.*, dehydration of ions as suggested by Le Blanc). Electrolyses with 25-cycle alternating current[8] showed that A requires 3/400 second to reach

[7] *Zeit. f. Elektrochem.*, 17, 699 (1911).

[8] In Fig. 7, the lower horizontal is the zero voltage line and the upper the calibration line (0.538 volt); the fainter wave gives the instantaneous current, through the cell, and the heavier the potential difference between the rotating electrode and an auxiliary electrode. The r.m.s. current was 1.80 amp.; the electrolyte contained 0.904 Cu per litre and was 7.6 N with respect to sulphuric acid; the temperature of the electrolysis was 18°C.

its maximum in the cathode beat, instead of jumping to it at once as it does with constant current. Electrolyses with a combination of direct and 25-cycle current showed that the time required for A to reach its maximum is fairly independent of the current, and that it does not reach the value zero until the electrode has been anode 1/200 second. These results made it probable that with increasing rapidity of the alternations the overvoltage would decrease, a conclusion that was borne out by measurements with

FIG. 7.

60-cycle current; while with 500-cycle alternating current, no overvoltage could be observed. A number of electrolyses in which the current was interrupted for varying periods between its changes of direction, gave a means of measuring the time required for the electrode to recover its normal state.

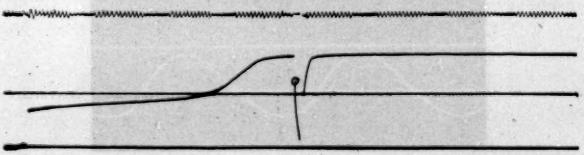
The time required for the overvoltage to "die away" when the current is shut off, was studied by interrupting the current for 1/85 second and measuring the rate of fall of potential difference (Fig. 8).[9] In that short time, the polarization fell to one-eighth of its value (0.66 volt) at the moment of interruption; the copper concentration at the cathode rose from 0 to 0.137 g. per litre, but instead of the calculated value $A + B \log z_0/z = 0.32$, only 0.08 volt was observed, which is less than half the second term alone. Such results show the futility of attempting to study these overvoltages by a commutator method.

In the example quoted (Fig. 8), hydrogen was already being evolved when the current was interrupted; but qualitatively identical results were obtained when the interruption was made while

[9] The electrolysis recorded in Fig. 8 was carried out at 18° C. with a current of 1.50 amp. and a calibration voltage 0.538. The electrolyte contained 2.016 g. Cu per litre of 7.6 N sulphuric acid. The distance from the curve to the small circle gives the $i.r$ drop.

only copper was coming out. To show that the minute current through the oscillograph element was not responsible for the loss of overvoltage, measurements were made with shunts in parallel with the element; although the current was thereby increased as much as thirty-fold, the rate at which the voltage died away was not appreciably affected. From measurements on the oscillogram, the number of coulombs that passed through the cell during the fall of voltage could be calculated; they showed that while the voltage falls to one-quarter its initial value, the current passing

FIG. 8.



through the oscillograph will dissolve from the electrode a layer of copper less than one-tenth atom thick. All these results fortify the conclusion that the "instantaneous overvoltage" must be due to some change which takes place in the deposit on the cathode and is independent of the current through the cell.

In the hope of reaching similar definite conclusions as to B, some hundreds of measurements have been made with solutions of the copper chlorides. We find it easier to invent explanations than to check them.

SUMMARY.

The concentrations at the electrodes during electrolysis were calculated by the diffusion theory of Weber, using the equations developed by Rosebrugh and Lash Miller. The periods of time required to liberate hydrogen from acid solutions of copper sulphate or of the copper chlorides in a large number of electrolyses, with constant, interrupted, successive, and sinusoidal currents, are in complete agreement with the predictions of the equations.

Adopting the concentrations given by these equations as basis for computing the concentration-voltages, the cathodic overvoltages during the electrolysis of acid solutions of copper sulphate have been determined by the oscillograph. There is definite evi-

dence of the absence of any "transfer resistance." The overvoltage may be expressed by the equation:

$$\text{Overvoltage} = A + (B - 0.03) \log z_0/z.$$

(z_0 being the copper concentration in the body of the electrolyte and z that at the cathode). Experiments show that B is independent of the concentration of copper and of acid, and also of the current-density down to 0.1 amp. per sq. dm. They also show that A is independent of the copper concentration, but increases with increase in the acidity; and that it falls to zero with the current-density and (in maximum conducting sulphuric acid) reaches a maximum value at 0.7 ampere per square decimeter, which it retains at higher current-densities. With less acid in the electrolyte, the maximum value of A is somewhat lower.

The quantity A, the "instantaneous overvoltage," which is the only part of the overvoltage studied heretofore, depends on the previous history of the electrode, and has less than its normal value for a measurable time after the electrode has been anode. The fall in overvoltage when the current is interrupted is too rapid to be measured by the commutator method; its rate is independent of large changes in the current passing through the measuring instrument.

Most of the decisive results of this investigation have been secured by Mr. A. R. Gordon during the past two years, but these results could not have been obtained without the foundation laid by former students in this laboratory. Neither Mr. Gordon nor I should like to see them published without an acknowledgment of the essential part played by Mr. L. V. Redman, now Vice-president of the General Bakelite Company; Mr. S. Dushman, of the Research Laboratories of the General Electric Company; Mr. J. T. Burt-Gerrans, now Associate Professor of Electrochemistry in the University of Toronto; Mr. H. A. G. Willoughby, now Principal of the Owen Sound Collegiate Institute; Mr. A. D. Hone, now Principal of the Technical High School of London, Ontario; and Mr. H. R. Brant, Director of Laboratories of the Ames Holden Tire and Rubber Company, Kitchener, Ontario. These gentlemen anticipated many of the relations now definitely established; they worked out the experimental details and to a large extent constructed the complicated apparatus without which this investigation would have been impossible.

Reconstruction of the Explosion Motor of the Niepce Brothers from 1806. P. CLERGET. (*Comptes Rendus*, March 23, 1925.)—The brothers, Nicephore and Claude Niepce, made a boat run on the Saone in 1806 by the combustion of lycopodium powder. On December 15th of that year Lazare Carnot, the famous "organizer of victory," and Berthollet rendered a report upon the machine to the Academy in Paris. In spite of the discarded term, caloric, we can readily understand their formal judgment. "In the apparatus of Messrs. Niepce no part of the caloric is dissipated in advance. The active force is an instantaneous product and the entire effect of the combustible is used to cause the expansion which serves as the active force." The two reporters cite experiments witnessed by themselves in which a simplified machine worked with lycopodium powder or with powdered coal mixed with resin.

The French Technical Aeronautics Service entrusted to M. Clerget the reconstruction of the Niepce machine, for which the patent was granted July 20, 1808. The drawings are so clear and comprehensive that it was possible to reproduce the motor with little difficulty. The machine worked well. With 5 cg. of lycopodium a weight of 20 kg. was lifted 30 cm. This gives an efficiency of 4 per cent. with the machine cold. For the wick used in the original machine to explode the mixture a wire heated by the current was substituted. The author holds that to the Niepce Brothers must be conceded the following, the use of powdered combustibles fed mechanically by a rotary distributor and the injection of the fuel into the combustion chamber with the aid of compressed air. In these two points he holds that the Diesel patents of 1892 and 1894 were anticipated.

The Niepce Brothers tried also to employ petroleum but failed. For Nicephore Niepce is claimed the distinction of inventing photography and a statue in his honor adorns Chalons sur Saone, where he was born in 1765. In the museum of that town the reviewer was disappointed by failing to find any exhibit of his photographic work.

G. F. S.

ERRATUM.

A SINGLE STRAIGHT CONDUCTOR AS A NEW FUNDAMENTAL.

BY

Carl Hering, D.Sc.

Member of the Institute.

(JOURNAL OF THE FRANKLIN INSTITUTE, February, 1925, page 235.)

Page 243, delete lines 4 to 13 inclusive, the sentence beginning with "Calculating the energy" and continuing to "is not rigidly exact."

SOME MEASUREMENTS OF THE SPECTRAL COMPONENTS OF PLANETARY RADIATION AND PLANETARY TEMPERATURES.*

BY

W. W. COBLENTZ.

Physicist, Bureau of Standards.

AND

C. O. LAMPLAND.

Astronomer, Lowell Observatory.

ABSTRACT.

THE OBJECT of the present paper is (1) to describe further measurements of the radiation emitted by planets; (2) to give an account of some preliminary attempts at separating this planetary radiation into spectral components; and (3) to give estimates of planetary temperatures.

By means of a series of transmission screens of water, quartz, glass, and fluorite the radiation emanating from the planets, *e.g.*, Mars, was separated into spectral components and the radiation intensities determined in the spectral regions of 0.3μ to 1.4μ, 1.4μ to 4.1μ, 4.1μ to 8μ, 8μ to 12.5μ, and 12.5μ to 15μ.

Radiometric measurements were made on Venus, Mars, Jupiter, Saturn, Uranus, the Moon and on terrestrial sources.

The results obtained verify our previous observations showing that the planetary radiation emanating from Jupiter and from Saturn, and transmitted by our atmosphere, is very small, while the planetary radiation from Venus, Mars and the Moon is, relatively, very intense.

The measurements on Venus were made when the bright phase was a narrow crescent. Under these conditions the dark part was found to emit an intense planetary radiation, amounting (per unit area) to 10 per cent. that of the total radiation from the bright crescent. Moreover, the southern hemisphere was found to be hotter than the northern hemisphere, just as was previously observed on Mars. Whether this is owing to physical differences in the surface, or owing to different climatic conditions

*Communicated by Doctor Coblentz and published by permission of the Director of the Bureau of Standards.

as a result of a seasonal variation in the inclination of the poles to the Sun, remains to be determined.

The measurements on Mars show that the bright regions are cooler than the dark regions, that the sunrise side of the planet is at a lower temperature than the side exposed to the afternoon Sun, and that the polar regions are cold, emitting no planetary radiation.

An estimate of the temperature of the irradiated surface of Mars was obtained as follows: (1) By direct comparison of the spectral components of the planetary radiation from Mars and the Moon, temperatures were obtained ranging from 5° C. for the bright equatorial regions to 20° C. for the adjoining dark regions; (2) by comparison of the observed spectral components of the planetary radiation from Mars with similar data calculated from the laws of spectral radiation of a black body, temperatures were obtained ranging from −15° C. for the bright regions to 12° C. for the dark regions; and (3) by calculation using the fourth-power law of total radiation, giving temperatures of −5° C. for the bright regions up to 15° C. for the dark regions.

When there was no phase on Mars the temperature of the east limb, or sunrise side, was −45° C. and that of the west limb 0° C. The temperature of the north polar region, during the winter season was down to −75° C. When there was early summer on the southern hemisphere, the temperature of the south polar region as viewed through the Martian atmosphere was −60° C. and in late summer it was +12° C., or even higher. The temperature of the night side of Mars may be down to −70° C.

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VI. Summary.

I. INTRODUCTION.

In previous communications [1] were given some preliminary measurements of planetary radiation, isolated by means of spectral transmission screens.[2] It was emphasized that these papers presented the results of a search for a means of investigating the radiation, particularly from the interior, of a planet.

The results obtained at that time showed that, for planets having dense atmospheres, the secrets within remained hidden. On the other hand, in the case of a planet like Mars, a way was shown for studying the radiation from different parts of the surface.

In view of the fact that the planetary radiation measurements of 1922 were undertaken with the expectation of renewing them in 1924, no attempt was made, at that time, to provide complete

[1] *Bur. Standards Sci. Papers* (No. 460), 18, p. 535, 1923. *Lowell Obs. Bull. No. 85.*

[2] *B. S. Sci. Papers* (No. 438), 17, p. 725, 1922.

equipment, including new transmission screens; also radiometer windows of rock salt, which is transparent farther into the infrared than fluorite, and, hence, transmits a greater spectral range of planetary radiation.

This, of course, was known to us at the time. But from the solar spectrobolometric data published by Fowle [3] it was evident that, for a preliminary trial of instruments and methods of measurement of planetary radiation, it would be immaterial whether the radiometer window was of fluorite or of rock salt. On the other hand, the question of permanence of the surface of the radiometer window was of the utmost importance, especially to one carrying his instruments 2500 miles from his laboratory. A slight blurring of the rock-salt surface, by moisture, will cause an appreciable scattering of the incident short wave-length radiation, with practically no scattering of the long wave-length radiation. This may reduce the total radiation intensity measurements by an amount comparable with that resulting from the use of a fluorite radiometer window which is opaque to the longest wave-lengths transmitted by rock salt. Furthermore the transmission measurements through the water-cell will not be comparable.

Such errors would be systematic, and should become detectable in the average of a prolonged series of measurements. Thus far these investigations have been of an explorative nature, mainly of instruments and methods of planetary radiometry. Hence, the refinements and completeness of equipment that naturally would be included in a permanent installation, devoted continuously to celestial radiometry, have not been attempted. Errors of observation preclude high accuracy and may obscure small, but real, differences in radiation intensities. Prolonged, systematic measurements will be necessary in order to establish small differences in radiation intensities, such as mentioned in previous papers.[4]

In previous papers [5] especial emphasis was placed upon the observation that red stars emit three to four times as much total radiation as blue stars of the same visual magnitude. One object in emphasizing this fact was to contrast the magnitude of a

[3] FOWLE: *Smithsonian Miscell. Coll.*, 68, No. 8, p. 41 (Fig. 13), 1917.

[4] *B. S. Sci. Papers* (No. 438), 17, p. 737, 1922. *Lowell Obs. Bull. No. 85.*

[5] *B. S. Bulletin* (No. 244), 11, p. 613, 1914. *B. S. Sci. Papers* (No. 438), 17, p. 726, 1922. *Pop. Astron.*, 31, p. 105, 1923.

star on the basis of its visual brightness (which depends upon the radiant luminous efficiency of the eye) with its radiometric magnitude,[6] as observed with a non-selective radiometer.

In a recent paper by Stetson [7] comment is made on this special emphasis placed on the wide difference in the total radiation of stars of the same apparent magnitude but of contrasting spectral types. He then points out that there is no reason for being surprised at this fact because, on the basis of modern ideas of stellar evolution, the giant red (*M* type) stars, such as Betelgeuse, must have many times the surface area of the smaller, the hotter, *A* type stars, such as Sirius.

In view of these comments, as well as others received in private communications, it is desirable to emphasize, as has been done in previous papers, that when the measurements are made in connection with a transmission screen the results obtained with the thermocouple are independent of the size and the distance of the star. It is the manner in which the energy is distributed throughout the spectrum (the spectral emissivity) that is noted by the radiometer. The importance of this fact cannot be too strongly emphasized. For it shows that the spectral energy distribution of red stars is markedly different from the blue stars, and it verifies the observations made without the cell. The water-cell transmits 30 to 40 per cent. of the total radiation from a red star, and 75 to 80 per cent. of a blue star, whatever its size or distance.

When the thermocouple is used without the water-cell or other transmission screens, its response depends upon the size and distance (as well as the temperature) of the star, and, as recently shown by Stetson (*loc. cit.*), it is a useful instrument in determining the diameter of stars. The fact that he was able to calculate the diameter of stars on the basis of the radiation laws seems to show that for the stars used in his calculations, the radiation emitted is not markedly unlike that of a black body, as he has assumed. This is an important deduction. For, when the data were obtained, some five to ten years ago, the question arose

[6] Some writers use the term "bolometric magnitude." Since the bolometer is one of several non-selective radiometric instruments that may be used to determine the total radiation intensity of a star evidently "radiometric magnitude" seems more appropriate.

[7] STETSON: *Pop. Astron.*, **31**, p. 230, 1923.

whether the high water-cell transmissions, observed on the hotter, more dense blue stars, as compared with the red stars, was owing, in part, to a high selective emission, such as obtains in incandescent platinum (or the acetylene flame) which has a very low spectral emissivity of infra-red rays. It is well known that the total radiation from a body (platinum is cited as an example) having a low selective emission of infra-red rays, is much less than that of a black body (a gaseous body of great size) at the same temperature. Such information appeals to the physicist even though the application may not be apparent in astronomy. A blue star, having a low selective emission of infra-red rays, would cool more slowly than an exactly similar one emitting non-selectivity like a black body. Hence the question raised in a previous paper [8] as to whether the transition time of a star, in the blue stage of its development, would be much longer when there is a suppression of the infra-red (relative to the visible) rays than when it radiates like a black body at the same temperature, may not be so absurd as a recent reviewer [9] of the whole subject would have it appear. For, while it is true that some of the hottest stars appear to have a spectral energy distribution which is closely that of a black body, there are instances where the spectral emissivity is highly selective.

The stellar thermocouple radiometer may yet prove useful in checking stellar classifications. For example, in a previous paper [10] it was shown that in the case of the binary star, Sirius, the water-cell transmission (65 per cent.) is inconsistent with the older stellar classification which places the primary star and its companion in class A_0, which stars have a transmission of about 80 per cent. The water-cell transmission indicates that the spectral type of the companion star of Sirius must be much lower than A_0—below type K (transmission = 50 per cent.), and more likely as low as type M (transmission 35 to 40 per cent.). In a recent paper by Eddington [11] the statement is made that the companion star of Sirius is given as F_0, but not accepted without demur because of the large density involved. As an alternative he suggests a low effective temperature, probably below Md, which, as

[8] *B. S. Sci. Papers* (No. 438).

[9] BRILL: *Ergeb. der Exakt. Naturwissensch.*, **3**, p. 33, 1924.

[10] *B. S. Sci. Papers* (No. 438), 17, p. 744, 1922.

[11] EDDINGTON: *Mo. Notices*, R.A.S., **84**, p. 322, 1924.

just noted, is in agreement with the radiometric observations. He mentions the companion star of Procyon as probably also being in class *M*, which is in agreement with the radiometric measurements with the water-cell.

From the foregoing it appears that, instead of using the theories of stellar evolution to explain some of the radiometric measurements, to those in doubt about the adequacy of the theories, these radiometric data may be of significance in substantiating the validity of some of the assumptions upon which these theories are based.

1. DISCUSSION OF PLANETARY RADIATION.

As fully set forth in a previous paper,[12] planetary radiation is predominantly of long wave-lengths, 5 to 25μ, the part transmitted in greatest abundance by the earth's atmosphere being of wave-lengths extending from 8 to 15μ.

In the case of a planet like Mercury, which becomes highly heated, radiation of wave-lengths 3 to 6μ, of perceptible intensity, will be emitted; and it is conceivable that small amounts of radiation of these wave-lengths penetrate our atmosphere. This will be mixed with reflected solar radiation, and hence is not distinguishable from the latter.

In the case of a planet, like Jupiter, having a dense atmosphere, as indicated in previous papers, the radiation emitted will be principally of wave-lengths from 4 to 8μ and 15 to 30μ. Since these emission bands coincide with the wide regions of high spectral absorption by the earth's atmosphere, but little planetary radiation will be transmitted to the earth's surface. Hence, it is to be expected that but little planetary radiation will be perceived by our instruments; which is in agreement with observations. The logical interpretation to be given to our measurements is that Jupiter is in radiative equilibrium, as the result of emission of low-temperature thermal radiation, which, however, is not observable because of its almost complete absorption by the earth's atmosphere. In this connection reference should be made to a highly suggestive and instructive paper on atmospheric radiation by Very,[13] which gives illustrations of the spectral emission and absorption of the earth's atmosphere.

[12] *B. S. Sci. Papers* (No. 460), 18, p. 537, 1923. *Lowell Obs. Bull. No. 85.*

[13] VERY: "Atmospheric Radiation," Bull. G, U. S. Weather Bureau, Publ. No. 221, 1900.

The measurement of planetary radiation is essentially a measurement of the heat interchange between the planet and the radiometer receiver, which in this case is a thermocouple of two symmetrically constructed receivers.

The *incoming* radiation from the planet is composed of reflected solar radiation, which terminates practically at 8μ, and planetary radiation which consists principally of wave-lengths 8 to 15μ. The intensity of this planetary radiation varies, of course, with the temperature of the planet.

The *outgoing* radiation from the thermocouple receivers is similar to the nocturnal radiation from black objects, which, on clear nights, may be 0.1 gr. cal. per cm.^{2} per min. When it is provided with a fluorite window, there is heat interchange between the radiometer receiver and the window, for wave-lengths greater than about 13μ. When the window is of rock salt, radiation of all wave-lengths to 25μ can escape from the radiometer window into the air. A certain percentage of the radiation of wave-lengths 8 to 15μ presumably escapes through the earth's atmosphere into space, and, theoretically at least, is focused upon the planet under investigation.

In ordinary laboratory thermometry, the two junctions of the thermocouple are placed in some constant temperature bath to determine the zero reading of the galvanometer. Then leaving one thermojunction in the ice bath, the other junction is placed in the material of which the temperature is to be determined. The resulting galvanometer deflection will be negative, positive or zero depending whether the temperature of the object is lower, higher or the same as that of the ice bath.

It is, of course, impossible to place one thermojunction in the isothermal layer of the earth's atmosphere, which is at a temperature of about $-70°$ C., and thrust the other junction out upon the surface of the planet, and thus determine its temperature from the indications of the galvanometer. However, by placing a thermocouple at the focus of a concave mirror, it is practicable to expose the two junctions to the sky and obtain a zero reading of the galvanometer. Then one junction is exposed to the image of the planet, and from the intensity of the radiation exchanges (instead of thermal conduction) and an application of the laws of radiation we can form some estimate of its temperature. Thus

far, our observations have not indicated a negative deflection, only zero or positive deflections when setting the thermojunction (receiver) from the sky upon the planetary image. This is probably to be expected, because the temperature of even the coldest planet is probably not down as low as that of interstellar space. Hence, if there is a radiation exchange, of wave-lengths 8 to 15μ, through the earth's atmosphere to space, it would affect both thermojunctions when they are exposed to the sky; but less radiation would be emitted from one of them when it is exposed to the planet. The result would be a slight positive, or no perceptible, deflection of the galvanometer needle. This seems relatively unimportant in comparison with the fact that the observations serve to establish an upper temperature level of $-70°$ C. to $-100°$ C. when there is no perceptible deflection on exposure of the thermojunction from the sky to the planet. Hence we have assumed a temperature of $-70°$ C. for the effective radiating layer of the atmosphere in order to translate into temperatures our water-cell transmissions which were higher than 40 per cent. The results obtained are in agreement with the calculations using the fourth-power law.

In concluding this discussion, it is of interest to obtain numerical data on the errors involved in assuming $-70°$ C. for the temperature of the isothermal layer, instead of some lower value, say 273° C., for interstellar space.

The total radiation, I, per cm.^{2} emitted by a black body at 14° C., $-70°$ C., $-120°$ C., and $-210°$ C. is 800, 200, 65 and 2 (arbitrary units), respectively. The percentage transmission of the radiation through the atmosphere, under our working conditions, was 19.0, 5.0, 1.4, and 0.00, respectively.[14] From this, it appears that about 20 per cent. of the radiation, of wave-lengths 8 to 15μ, from the thermocouple, at 14° C., escapes through the atmosphere into space. The maximum radiation, of wave-lengths 8 to 15μ, entering through the atmosphere, from an object at $-70°$ C., $-120°$ C. and $-210°$ C. is $I = 10$, 1 and 0, respectively. The intensity of the incoming radiation at $-70°$ C. is only about 5 per cent. of that escaping from the thermocouple into space.

But this is not the only thing to be considered. For, when using a rock-salt window there is a constant fluctuation of the

[14] MENZEL: *Astrophys. Jr.*, **58**, p. 70, 1923.

zero reading of the galvanometer which seems to be caused by variations in transparency of the air for the outgoing radiation from the thermocouple receiver to interstellar space. That this is so is easily shown by inserting the screen of fluorite or thin glass. The intensity of the incoming radiation from a celestial object at −70° C. or lower is very small, and atmospheric conditions, even in the high, dry climate of the Lowell Observatory, must be steady in order to attain an accuracy of 5 per cent. A lower altitude and greater humidity would no doubt suppress this effect. Hence, it appears that unless the temperature of the celestial object is up to about −75° C., its presence cannot be determined with certainty from the water-cell transmission, by exposing the thermocouple to the sky and to the object, which is the method usually employed in making the observations.

The observation of temperatures that are considerably higher than the previously calculated mean values is not necessarily erroneous. The thermocouple responds to thermal radiation which emanates from the hottest spots on the planet. These hot areas are not the highest peaks which are exposed to air convection, but the depressions and cracks in the surface where convection is a minimum and the heat absorbed from the Sun is retained. This is repeatedly observed at Lowell Observatory, Flagstaff, Ariz. (elevation 7250 ft.), and at the rim of the Grand Canyon of the Colorado River (elevation 6900 ft.) where even the darkest colored rocks and soil were only perceptibly warmed by the Sun. On the other hand, the spots that were shielded from air-currents became highly heated. For example, in a narrow canyon on the brink of the Colorado River (some 6000 ft. below the rim) the rocks were uncomfortably hot to the touch. In fact, samples of granite that were collected had to be cooled in a stream of water in order that they could be comfortably carried in the pocket.

It is to the radiation emanating principally from the highly heated areas, scattered here and there over the surface of the planet, that the thermocouple responds. The cooler areas contribute also to this extremely heterogeneous radiation, but the amount so contributed will no doubt be small, owing, in part, to the long wave-lengths emitted, which are not transmitted by our atmosphere.

II. APPARATUS AND METHODS.

The successful application, in 1921, of the method of determining the temperatures of stars by separating their radiation into spectral components by means of transmission screens [15] foreshadowed a similar application to planetary temperatures, especially that of Mars at the opposition of 1924. In the meantime it seemed desirable to undertake a survey of the problem and, in 1922, a few preliminary measurements [16] were made, preparatory to this year's work. From the experience gained, the apparatus was suitably adapted to the particular problems to be studied. These preliminary tests showed that, since the planetary radiation which is transmitted by the atmosphere is principally of wave-lengths 8 to 15μ, the most promising results would be obtained by separating this radiation into two, approximately equal, components, of wave-lengths 8 to 12.5μ, and 12.5 to 15μ, by using a fluorite screen of a suitable thickness.

The essential details of the radiometric apparatus as used in the present investigation are as follows: For details of construction of the iron-clad Thomson galvanometer [17] and the thermocouples, reference may be made to previous papers on this subject.

The galvanometer coils, of 20 ohms each, were connected all in parallel to give a resistance of 5 ohms, as used in the researches of 1914 and 1922. The mirror was an especially fine one which permitted reading the scale at a distance of 2 metres. Under these conditions the current sensitivity was $i = 1.7 \times 10^{-10}$ amp. for a single swing of 3 sec. It is relevant to add that by using a lighter magnet-system and a smaller mirror a higher sensitivity would have been attainable. The present system was adopted as the result of long experience with earth tremors, and general unsteadiness resulting from magnetic and electrostatic disturbances in mountain stations.

The radiometric apparatus was used in connection with the 40-in. (100 cm.) reflector of the Lowell Observatory, as described in previous papers. The galvanometer stood on a concrete pier in the newly constructed silvering room, which is partially under ground and situated at one side of the observatory dome. This

[15] COBLENTZ: *B. S. Sci. Papers* (No. 438), 17, p. 726, 1921.
[16] COBLENTZ: *B. S. Sci. Papers* (No. 460), 18, p. 536, 1923.
[17] *B. S. Bull.* (No. 282), 13, p. 423, 1916.

eliminated the difficulties of unsteadiness from wind, cold air-currents, etc., which were previously experienced.

Some of the measurements were made using the single flat diagonal mirror (Newtonian arrangement), the outfit having a focal length of 18.4 feet. For most of the measurements on Mars a third mirror was introduced, giving a focal length of 53.3 feet. Under these conditions the image of Mars was about 2 mm. at opposition, and when using the smallest receiver it was possible to make eight isolated radiometric measurements across the disc.

1. DESCRIPTION OF THE THERMOCOUPLES.

The vacuum containers for the thermocouples were of the same general design as used in the previous measurements of stellar and planetary radiation.[18]

The thermocouples in containers Nos. 7, 11 and 12 remained unchanged as used in the planetary radiation measurements of 1922.[19]

Container No. 11 was No. 8 used in 1921, but with thermocouples of pure bismuth wire 0.025 mm. in diameter and platinum-rhodium wire 0.020 mm. in diameter.

The bismuth wire was 3 mm. long, kept straight in order to prevent radiation from falling on both receivers when the planetary image was focussed on one of them. The resistance of thermocopule No. 1 was 7.7 ohms, the diameter of the receivers being 0.28 mm. The resistance of thermocouple No. 2 was 5.5 ohms, the receivers being 0.23 (the left-hand one, No. 11-2l in the tables) and 0.27 mm., respectively. The receivers were small globules of tin, attached to the Pt-Rh wire and pressed flat between glass plates as described in previous publications. These receivers were not so large in diameter as those used three years ago and attained temperature equilibrium in 2 to 3 seconds (instead of 8 to 10 seconds), which was the time of swing of the galvanometer needle. The window was of rock salt 4 mm. in thickness.

Container No. 12 was the old mounting No. 9 used in 1921, but with new thermocouples of 0.025-mm. bismuth wire and of 0.020-mm. Pt-Rh alloy wire. The bismuth wire (length 2.5 to 3 mm.) was bent U-shaped in order to bring the receivers close

[18] *B. S. Sci. Papers*, Nos. 244, 438 and 460.

[19] *B. S. Sci. Papers* (No. 360), 18, p. 538, 1923.

together, so that the star image could be quickly changed from one receiver to the other receiver. The resistance of thermocouples Nos. 1 and 2 were 4.7 and 4.4 ohms, respectively; the diameters of the receivers (of tin pressed flat) were 0.31 and 0.32 mm., respectively. In container No. 12 the fluorite window was replaced by one of rock salt about 4 mm. in thickness and 25 mm. in diameter.

Container No. 13 was the old mounting No. 10 used in 1922, but with a rock-salt window and with thermocouples of straight bismuth wire and 0.020-mm. Pt-Rh alloy wire. Thermocouple No. 1 was made of bismuth 0.07-mm. wire, pressed flat, with receivers of pure tin 0.018 mm. in thickness and 1.17 mm. in diameter. The resistance was 1.2 ohms. In spite of the large size of the receivers this design was quick-acting, attaining a temperature equilibrium in 5 to 6 seconds.

Thermocouple No. 2 was made of pure bismuth wire 0.025 mm. in diameter with receivers of tin 0.65 and 0.66 mm., respectively, in diameter. The resistance was 7.3 ohms. The receivers were of large diameter in order to intercept the entire planetary disc.

2. PRESERVATION OF THE ROCK-SALT WINDOWS.

The surfaces of the rock-salt windows were optically flat, and had an excellent polish.[20] Before mounting them they were kept in a desiccator. They were attached to the vacuum thermocouple containers by means of the vacuum stopcock grease described in previous papers.[21]

Immediately after mounting these windows, a small amount of stopcock grease (beeswax and mutton tallow) was placed around the edge of the outer surface and another window of fluorite (or glass) pressed upon it. The stopcock grease provides an air-tight adhesive which does not corrode the rock salt; and it can be easily wiped off without blurring the surface.

To prevent slipping in transportation, a small amount of beeswax was melted around the edge of this double window.

When it was desired to observe planetary radiation through only the rock-salt window, the outer one of fluorite was easily lifted off; and it was as easily replaced at the conclusion of the observations.

[20] Prepared with great care by Mr. Clacy, of the Bureau of Standards.

[21] *B. S. Sci. Papers*, Nos. 244, 438 and 460. *Lowell Obs. Bull. No. 85.*

A supply of rock-salt windows has been preserved for some time by enclosing them between plates of glass and melting some beeswax around the edge. This seems to promise a simple solution of the problem of polishing rock-salt windows and shipping them to their destination.

3. DESCRIPTION OF THE TRANSMISSION SCREENS.

The function of the transmission screens for separating stellar radiation into spectral components was described in a previous paper.[22]

It was there shown that, in order to provide a sharp cut-off such as would be obtained by dispersing the radiation into a spectrum and shutting out part of it by means of a knife-edge screen, it is desirable to use screens having a uniformly high transmission over a given region of the spectrum, and terminating abruptly in complete opacity in the rest of the spectrum. In this manner, should the occasion arise, it will be possible to compare spectral energy measurements, obtained by the two methods, without making long, tedious, and perhaps uncertain, corrections. It was with this object in view that the previous measurements on stellar radiation were made in this manner.

In the case of planetary radiation it is convenient to modify the previous experimental procedure. The spectrobolograms published by Fowle[23] show that between 6μ and 8μ practically no solar radiation is transmitted through the earth's atmosphere, while the part transmitted in the transparent region lying between 8μ and 15μ is only about 0.1 per cent. of the total incoming solar radiation of all wave-lengths. Our preliminary measurements, of 1922,[24] show that for the Lowell Observatory station (elevation 7250 ft.) the solar radiation of wave-lengths greater than 4.1μ is only 0.4 per cent. of the total incident radiation of all wave-lengths.

From this it appears that it is immaterial whether one uses a transmission screen (quartz, of proper thickness) which has a sharp cut-off at 4.1 or a screen like glass which is spectrally more attenuated in its transmission.

Fortunately, this spectral transmission of thin sheets (0.1

[22] *B. S. Sci. Papers* (No. 438), 17, p. 733, 1922.
[23] FOWLE: *Smithsonian Miscell. Coll.*, 68, p. 41, 1917. (See Fig. 13.)
[24] *B. S. Sci. Papers* (No. 360), 18, p. 557, 1923.

to 0.2 mm. in thickness)[25] of glass terminates at 8μ, and hence coincides closely with the limit of atmospheric transmission in this part of the spectrum. A thin sheet of glass is therefore well adapted for a screen, in planetary radiation measurements. Mica does not seem so well adapted for this purpose, thin sections transmitting radiation at 11 to 14μ.[26]

For the present investigation[27] the following transmission screens were used:

Rock salt, which was used as the window of the vacuum thermocouple container (thickness 4 to 5 mm.), has a uniform transmission of about 91 per cent. to 15μ, beyond which point its transmission gradually decreases to complete opacity beyond 23μ.[28] Since the atmosphere acts as a transmission screen which is completely opaque to radiation of wave-lengths greater than 15μ, the rock-salt window does not obstruct, selectively, any of the incoming radiation.

Fluorite, thickness 2.7 mm., has a high transmission[29] (91 per cent.) throughout the spectrum to 8μ. Beyond this point this particular screen has the transmissions given in Table VII.

By means of this screen it was possible to determine the planetary radiation extending from 12.5 to 15μ, which, as already stated, is practically the spectral limit of transparency of the atmosphere. It seems preferable to use 15μ instead of 14μ, as the practical long wave-length limit in view of the fact that Fowle's[30] solar spectral energy curves show radiation transmitted beyond 14μ. For low-temperature radiation this part between 14μ and 15μ may be an appreciable portion of the total planetary radiation of wave-lengths between 8μ and 15μ.

Glass, thicknesses 0.158 and 0.23 mm., respectively, is opaque to radiation of wave-lengths greater than 8μ.

By inserting this screen in the path of the radiation incident upon the thermocouple receiver a measurement is obtained of the total planetary radiation which is transmitted by the earth's atmosphere.

[25] "Investigations of Infra-red Spectra," *Publ. No. 65,* p. 64 (Fig. 52), 1906; and *No. 97,* p. 45 (Fig. 29), 1908, Carnegie Inst. of Washington.

[26] *Carnegie Publ. No. 65,* p. 49.

[27] See preliminary communication in *Publ. Astronom. Soc. Pacific,* 36, p. 220, 1924.

[28] RUBENS and TROWBRIDGE: *Ann. der Phys.* (3), 60, p. 724, 1897.

[29] *Publ. No. 97,* p. 45, Carnegie Inst. of Washington, 1908.

[30] FOWLE: *Smithsonian Miscell. Coll.,* 68, p. 41, 1917. (Fig. 13.)

This measurement and the one obtained through the fluorite screen (when both are corrected for reflection) are sufficient to separate the planetary radiation into two spectral components, extending from 8 to 12.5μ and from 12.5 to 15μ, respectively.

Quartz, thickness 4.77 mm., is transparent to all wave-lengths from the extreme ultra-violet to 4.1μ in the infra-red.[31]

The difference in the transmission of the quartz and the thin glass screens (corrected for reflection, of course) is a measure of the radiation (mixed solar and planetary) extending from 4.1 to 8μ.

The measurements show that the quartz-cell could be used instead of the glass without affecting the results. However, by using the two screens, useful data may be obtained on the variation of atmospheric transmission with humidity.

Water, thickness 1 cm., is opaque to radiation of wave-lengths greater than 1.4μ. It is therefore especially useful, in connection with the quartz screen, in determining the spectral component radiation extending from 1.4 to 4.1μ.

Since its successful use in 1914, the water-cell, 1 cm. in thickness, has been received with especial favor by astronomers as a transmission screen in celestial radiometry. However, unless a heating device is provided it cannot be used in very cold weather. There are but few substances, having great opacity beyond 1.4μ, which can be substituted for water. Among these are alcohol,[32] glycerine [33] and sulphuric acid; water solutions of these materials; also a water solution of sodium chloride or some other material which lowers the freezing point. Glycerine is especially useful since it undercools easily and remains liquid for a long time at temperatures far below freezing.

Substances having water of crystallization, *e.g.,* potassium-alum and selenite, could be used as a substitute for water in the liquid state. However, in order to absorb completely radiation of all wave-lengths greater than 1.4μ, it is necessary to use a layer of water at least 1 cm. in thickness.[34] Hence, in order to obtain a layer of water equivalent to 1 cm. in thickness in the free liquid state, it would be necessary to use crystal sections

[31] See transmission curves of quartz and of water in *B. S. Sci. Papers* (No. 438), 17, pp. 734 and 735, 1922.

[32] *Phys. Rev.,* 17, p. 51, 1903.

[33] *B. S. Sci. Papers* (No. 418), 17, p. 272, 1921.

[34] JOUR. FRANK. INST., 180, p. 355; 181, p. 233, 1916.

which are several times this thickness. This does not seem desirable in view of the large change in focus which occurs on insertion of the screen in the optical path.

Among the most useful, permanent, and easily obtainable substances, containing water of crystallization which is suitable for such a screen, is selenite.[35]

Another procedure would be to adopt a reproducible screen which, in a 1-cm. layer, is opaque to radiation of wave-lengths somewhat greater than 1.4μ—say at 2 to 2.5μ. Various oils[36] have a high transmission throughout the spectrum to 2μ.

Spectral Components.—By means of the rock-salt window, it was possible to obtain the total radiation of wave-lengths extending from 0.3 to 15μ, which are the extreme limits of atmospheric transmission. By means of the above-mentioned screens, it was possible to separate this radiation into spectral components extending from 0.3 to 1.4μ, 1.4 to 4.1μ, 4.1 to 8μ, 8 to 12.5μ, and 12.5 to 15μ.

A quick method of determining the radiation emitted by a planet is to note the percentage difference between the water-cell transmission of the direct solar radiation and that of the radiation emanating from the planet.

In concluding this discussion, it is relevant to emphasize that the planetary radiation is measured by the amount of the total incident radiation which is absorbed by the screen, although the data are usually recorded in the per cent. transmitted. While the data obtained with the water-cell are definite, in this year's work we have supplemented these measurements with others in which the spectral components of the planetary radiation, at 8 to 12.5μ and 12.5 to 15μ, is quite free from reflected solar radiation. By this means it is possible to obtain temperature estimates of the radiating surface of the planet without invoking the law of total radiation, the inverse square law of distance, etc., as has been done in previous calculations.

III. RADIOMETRIC MEASUREMENTS.

Under the present caption are given the essential details of the radiometric measurements; also tabulated data pertaining to

[35] *B. S. Sci. Papers* (No. 418), 17, p. 274, 1921. The low transmission in the region of 0.8μ is owing to scratches on the cleavage surface. See also *Sci. Paper No. 168*, p. 636.

[36] *B. S. Sci. Papers* (No. 418), 17, p. 267, 1921.

each planet observed. The accuracy attained in this year's measurements was as high as in previous years. Hence, for brevity, some of the details regarding the number of sets of measurements, the per cent. deviation from the mean, etc., are omitted from the tables.

1. THE SUN.

As mentioned on a preceding page, the water-cell and the quartz screen give the spectral components of the solar radiation lying between 0.3 to 1.4μ and from 1.4 to 4.1μ, respectively. Between 4.1μ and 8μ the radiation transmitted through the Earth's atmosphere will be mixed, solar and planetary, and an estimate is given of the planetary radiation of these wave-lengths.

As shown in a previous paper[37] the spectral component of solar radiation of wave-lengths 4.1 to 12.5μ amounts to only about 0.4 per cent. of the total. This value was obtained as the result of two closely agreeing measurements of the transmission through the quartz-cell on June 17, 1922, the separate values being 91.2 per cent. at 11:45 A.M., and 91.0 per cent. at 4 P.M. (M.S.T.). The mean value is 91.1 per cent., whereas the calculated value is 91.5 per cent.; a difference of 0.4 per cent. Since the reflection losses are probably greater than 8.5 per cent., the chances are that the above value is even less than 0.4 per cent. Of this amount perhaps 0.1 per cent. lies between 4.1μ and 8μ.

No solar observations were made this year. The spectral radiation components, observed in 1922, are given in Table III.

In a previous paper[38] attention was called to the observation that, in the short wave-lengths the spectral component radiation of α Aurigæ (Capella) is less than that of the Sun, although these two stars are of the same type. This result has been verified, since then, by Pettit and Nicholson,[39] and is in agreement with other methods of spectral comparison which show that dwarf stars are bluer than giant stars of the same type. Their measurements indicate a solar radiation component of 0[40] to 0.5[41] per cent. for wave-lengths lying between 8μ and 15μ.

[37] *B. S. Sci. Papers* (No. 460), 18, p. 557, 1922.
[38] *B. S. Sci. Papers* (No. 460), 18, p. 558, 1922.
[39] Carnegie Inst. of Washington, *Yr. Book No. 22*, p. 191, 1923.
[40] PETTIT and NICHOLSON: *Publ. Astronom. Soc. Pacific*, **35**, p. 196, 1923.
[41] PETTIT and NICHOLSON: *Pop. Astron.*, **32**, p. 76, 1923.

As already mentioned on a preceding page, an integration of Fowle's (*loc. cit.*) solar spectral energy curves gives a radiation component of about 0.1 per cent. for the spectral region of 8 to 15μ.

There is, therefore, a good agreement on this question, showing that the component of solar radiation in this region of the spectrum is extremely small, and is negligible in the case of planets like the Moon or Mars, which have a large planetary radiation.

The spectral components of solar radiation, corrected for reflection, used in the present paper, are as follows: 0.3 to 1.4μ = 75.5 per cent.; 1.4 to 8μ = 24.3 per cent.; 8 to 15μ = 0.2 per cent. The ratio of the first two components (24.3 ÷ 75.5 = 0.322) gives a ready means of determining the planetary radiation mixed with the solar radiation of wave-lengths extending from 1.4 to 8μ.

2. MERCURY.

Unfortunately at the time when the present series of planetary radiation measurements was in progress Mercury was not favorably situated for radiometric measurements. Recently Pettit

TABLE I.

Transmission of Planetary Radiation through a Cell of Water 1 Cm. in Thickness; Also the Percentage of Planetary Radiation Emitted. Values Are Not Corrected for Reflection of Quartz Windows of Water-cell.

Object.	Percentage Transmission.			Remarks.
	Mean Value, 1913.	Mean Value, 1922.	Mean Value, 1924.	
Sun	....	69.6	....	75.5 when corrected for reflection.
Mercury	....	....	6.9*	
Venus	59.3	63.6	63.1†	
Mars	....	47.3	47.1	Whole disc June 25, 1924.
			35.8†	
Mars: Northern Hemisphere	....	....	41.8	June 27, 1924.
Equator			39.1	
Jupiter	65.7	68.2	67.0†	
Saturn: Disc	55.0	60.2	62.3†	
Rings	....	64.5	....	
Uranus	....	....	70.0†	
Moon	14.7	....	11.6†	

*Observed by Pettit and Nicholson in 1923.

†Using a rock-salt radiometer window excepting Mars, for which a fluorite window was temporarily used as in previous measurements.

and Nicholson [42] have made some instructive radiometric measurements on Mercury. Since the method of construction of their vacuum thermocouples, as well as their methods of observation are practically duplicates of our own, their results are included in the present paper for completeness in exposition of the data on planetary radiation (Table I).

3. VENUS.

From a consideration of the results obtained and their probable significance astronomically, the radiometric measurements on Venus seem the most interesting of the whole series. The atmosphere of Venus is probably about as dense as that of the earth. It has a high albedo. Its period of rotation is in doubt.[43] There seems to be an absence of water vapor. To account for this it has been assumed that the water vapor is condensed on the unilluminated side of the planet.

Owing to its closeness to the Sun a high temperature must prevail. Menzel's [44] calculations, based upon our radiometric measurements of 1922, indicate a surface temperature of 50° C. That such a high temperature must prevail is shown by our measurements, which will be described under the present caption. Not only does the illuminated crescent of Venus show the presence of considerable planetary radiation, but the unilluminated part of the disc also emits a large amount of infra-red rays. This planetary radiation is highly selective, the most of it lying in the spectral region of 8 to 12μ.

How are we to account for this radiative condition? Water vapor is supposed to be absent; and if it were present it probably could not strongly emit radiation of wave-lengths 8 to 12μ. Other gases that may be present, for example N and O, have little or no absorption in this spectral region, and hence, at the temperature which probably prevails, cannot emit much radiation of these wave-lengths. Hence, if there is radiation from the gaseous envelope it must be emitted by CO_2 and (if oxygen is present) by ozone, which, owing to the proximity of Venus to the Sun, would be formed in great abundance, and which has a strong absorption band at 10.5μ. The rest of the planetary radiation

[42] PETTIT and NICHOLSON: *Publ. Astronom. Soc. Pacific*, **35**, p. 194, 1923.

[43] See a recent summary by CHARLIER: *Publ. Astronom. Soc. Pacific*, **36**, p. 105, 1924.

[44] MENZEL: *Astrophys. Jour.*, **58**, p. 65, 1923.

must emanate from the interior of the planet. These two sources of radiation will account for the planetary radiation emanating from the irradiated crescent of Venus.

But what is the mechanism that maintains a relatively high temperature on the unilluminated portion of the planet? If the rotation period is long (225 days), then it seems necessary to assume that the surface of Venus is still hot and emits its own proper radiation. Hence, whether the time of solar irradiation is long or short, the effect is of minor importance upon the unilluminated portion of the planet. The radiation from the heated gases which are supposed to pass, by convection, from the irradiated to the dark part of the planet, does not seem sufficient to account for the observations to be presented in this paper.

If the rotation period is short then, owing to the relatively dense atmosphere, the heat would be retained and reradiated for some hours after sunset, as obtains on this earth, which is less highly heated, owing to its greater distance from the Sun.

The fact that the southern hemisphere (the bright cusp as well as the adjoining dark region) is hotter than the northern (cusp and contiguous dark area) might be owing to a difference in surface conditions as observed on Mars. This difference in temperature may be owing, in part, to a tilting of the axis of rotation, a variation in insolation, and a consequent change in the seasons, as observed on the Earth and on Mars. If this is the case then, in the course of time, temperature conditions should be reversed and the northern hemisphere should become the hotter. This, as well as several other questions, cannot be answered without further observations extending over a long period.

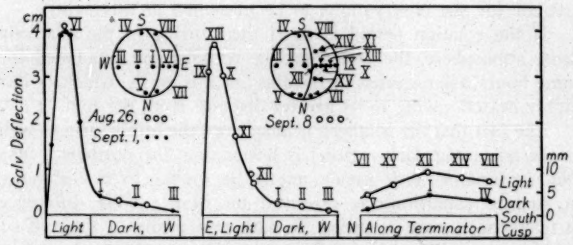
Equatorial Measurements.—Data pertaining to the various radiometric measurements on Venus are given in Tables I, II, and III. When the measurements were begun the illuminated part of the planet was still in the form of a well-defined crescent.

One series of measurements consisted in noting the galvanometer deflections along an equatorial diameter passing through the middle of the crescent, as shown by the roman numerals, I, II, III, etc., in the insert in Fig. 1. The observations of August 26th are depicted in circles (o o o), and those of September 1st in dots (· · ·). Some of the observations on the dark side of the planet were made in daylight, and it was found that, with the water-cell

in front of the thermocouple, a small deflection (0.02 to 0.1 cm., depending upon the intensity of the daylight) was obtained in making the setting from the sky to the dark surface. This was considered to be merely scattered light which did not emanate from the planet. It was observed to be practically the same for each setting on the planet and it was deducted from the observations made without the cell. The resultant data were found in good agreement with those obtained before daylight when practically no scattered light was observed.

The observations on different dates are in good agreement, showing that on the dark side of the planet, but at a sufficient

FIG. 1.



Radiation from light and dark regions on the disc of Venus.

distance from the terminator to avoid stray light from the bright crescent, the planetary radiation intensity (at this phase) was 10 per cent. that of the brightest part of the crescent, decreasing to 5 per cent. at a point half-way between the terminator and the dark limb. This reminds one of the nocturnal radiation from the earth which is about 10 per cent. of the solar constant.

The spectral components of the radiation emitted from the bright and the dark phase, for August 26th, are given in Table III. During the course of the observations of this morning, meteorological conditions were unusually steady and the galvanometer deflections could be accurately read to 0.1 mm. Hence, although the observed deflections were small, they were reliable. For the dark phase two series of data are given. The first series is based upon the direct observations, uncorrected for what is considered to be diffuse light. On this basis the water-cell transmission is 31 per cent., and that of the glass screen is 35.8 per cent. The observed galvanometer deflections, corrected for reflec-

TABLE II.

Water-cell Transmissions in Per Cent. of the Total Radiation Emanating from Isolated Regions on Venus. Also Radiation Intensity.

Region on Venus.	Aug. 26th.		Sept. 1st.		Sept. 2nd.		Sept. 8th.
	Radiation.	Transmission.	Radiation.	Transmission.	Radiation.	Transmission.	Radiation.
	cm.	p.c.	cm.	p.c.	cm.	p.c.	cm.
VII. North, bright cusp....	1.2	....	....	....	.44	69.2	.46
VIII. South, bright cusp....	1.5	....	....	....	.87	51.2	.73
V. North, dark, adjoining cusp.....	....	....	.15	....	.11	....	.12
IV. South, dark, adjoining cusp.....	....	....	.30	....	.18	....	.26
VI. Bright, middle of crescent.....	4.1	63.1	3.85	63.5	....	....	3.65
I. Dark, near terminator	....	....	.41	....	....	....	.28
II. Dark, midway between terminator and dark limb.....	....	....	.21	....	....	....	.18
III. Dark limb.....	....	....	.10	....	....	....	.08
XII. Mid-point on terminator.....	....	....	....	....	....	....	.92
XIV. Quarter point on terminator and south cusp.....	....	....	....	....	....	....	.81
XV. Quarter point on terminator and north cusp.....	....	....	....	....	....	....	.66

tion from the surfaces of the screens were, respectively, 1.3, 1.5, 3.3, and 4.2 mm., as observed through the water, glass, and fluorite screens, and the direct deflection. If we consider the deflections produced by the radiation passing through the water-cell as being caused by diffuse light (whether local, terrestrial, or diffused in the atmosphere of Venus) and deduct this value from the observations obtained through the glass and the fluorite screens, the resultant deflections are 0.2, 2.0 and 2.9 mm. This shows that practically no planetary radiation of wave-lengths shorter than 8μ is transmitted through the glass screen. As already disclosed [45] the planetary radiation of wave-lengths $\lambda 8$–15μ is highly selective, 62 per cent. (Table III) being of wave-lengths $\lambda 8$–12.5μ. This

[45] *Science*, **60**, pp. 295 and 318, 1924.

TABLE III.

Spectral Components of Planetary Radiation in Per Cent. of the Total Radiation Emanating from the Planet.

Object.	Date, 1924. M.S.T.	Thermo-couple.	Observed Spectral Components.			Solar and Planetary. λ1.4 to 8μ	Planetary Radiation.			Remarks.
			Fluorite λ0.3 to 12.5μ	Glass λ0.3 to 8μ	Solar. Water λ0.3 to 1.4μ		λ8 to 12.5μ	λ12.5 to 15μ	λ8 to 15μ	
Jupiter	June 20, 10 to 11 P.M.	No. 13-2	99.2	96.3	72.8	23.5	2.9	0.8	3.7	Receiver covers one-half of disc.
Jupiter	August 16, 8 to 9 P.M.	No. 13-1	....	....	74.6	....	....	....	1.2	53.3-ft. f. l. Receiver covers ½ of disc. Planetary radiation calculated from water-cell transmission.
Saturn	June 20, 8 to 10 P.M.	No. 13-2	96.5	....	66.9	....	....	3.5	....	
Saturn	June 21, 9 to 10 P.M.	No. 13-2	96.8	87.8	68.2	19.6	9.0	3.2	12.2	Receiver covers ball.
Venus	August 25, 5 to 5:30 A.M.	No. 11-2	93.6	80.5	68.4	12.1	13.1	6.4	19.5	53.3-ft. focus. Receiver covers about ¼ of central part of crescent.
Crescent	August 26, 5:30 to 6 A.M.	No. 11-1	97.0	85.3	63.1	22.2	11.7	3.0	14.7	
Dark side		No. 11-1	78.7	35.8	31.0	4.8	42.9	21.3	64.2	
Dark side		No. 11-1	....	....	....	6.9	62.1	31.0	93.1	After correcting for diffuse light.
Sun	June 17, 1922		...	...	75.5	24.3	$\frac{\lambda 4.1 \text{ to } 12.5\mu}{0.2}$	....	....	

high selectivity is also observable in the planetary radiation emitted from the bright side of Venus, from which it would appear that the extra heating by solar radiation has but little effect upon the spectral quality of the planetary radiation.

The water-cell transmission measurements on the bright crescent are in good agreement with similar measurements made in 1914 and in 1922. In making the measurements in 1914 (August 19th) the thermocouple receiver covered part of the unilluminated disc and the water-cell transmission is somewhat lower (59.3 per cent., see Table I) than measured since then when only the illuminated crescent was intercepted. The present measurements on the dark side of the planet explain this discrepancy. It seems rather curious that the measurement of the radiation from the dark part of Venus should be neglected all these years. For the low transmission of radiation through the water-cell, observed in 1914, is evidently owing to the radiation from the dark part of the planet.

North and South Polar Settings.—The position of the poles of Venus is unknown. Hence, the present designation means simply the regions near and including the bright cusps of the planet. The data are given in Table II. The direct galvanometer deflections, as well as the per cent. transmissions through the water-cell, are consistent in showing that the south cusp, as well as the unilluminated region adjacent to the cusp, is at a higher temperature than the corresponding positions near the north cusp. (Fig. 1.)

As mentioned on a preceding page, further investigations will be necessary to determine whether the higher temperature of the southern hemisphere is owing to a higher absorptivity of the surface for solar radiation or owing to different climatic conditions, caused by a periodic variation in the inclination of the axis of rotation to the sun, or to both factors. Evidently the thermocouple radiometer is a promising means for investigating the secrets which still remain hidden within the atmosphere of Venus, and it may be a means of determining the position of the poles as well as the period of rotation.

Mention has already been made of the presence of what appeared to be diffuse light, part of which was no doubt caused by scattering in the radiometric apparatus. But part of it may have been caused by diffusion from the bright into the dark

part of the atmosphere of Venus. For it was most marked in the measurements made along the line of the terminator, indicated by the roman numerals I, IV, V, and dropped to half intensity at the position III in Fig. 1. Such a diffusion or luminescence has been noticed, visually, by several observers. Further radiometric measurements should be made on this subject. If it is an auroral discharge then, it should be possible to establish the fact by means of the spectroscope.

To recapitulate, mention has already been made that the ratio of the spectral components $\lambda 8$–12.5μ:$\lambda 12.5$–15μ is closely the same for the irradiated and the dark portion of the planet. (Table III.) From this it appears that, whether the time of solar irradiation is long or short, the effect seems to be of minor importance upon the radiation from the dark portion of the planet.

There are inconsistencies in the views held concerning the constitution of the atmosphere of Venus, and the radiometric measurements which show that the planetary radiation is highly selective, the spectral components $\lambda 8$–12.5μ and $\lambda 12.5$–15μ having the ratio $A \div B = 2$.

If water vapor is absent from the atmosphere of Venus, then only CO_2 and ozone can do the absorbing (and the radiating at 10.5μ), and the rest of the absorption must occur at the surface of the planet. The observed ratio ($A \div B = 1.06$) of the spectral components of the planetary radiation from the Moon indicates the possibility of the surface and atmosphere of Venus emitting a planetary radiation having a ratio of the spectral components, $A \div B = 2$, as observed.

The theory of gaseous convection is not excluded. But with water vapor absent it does not appear that the radiation from CO_2 and ozone (which would occur at the higher atmospheric levels) is sufficient to account for the observations. For, if the radiation from the dark regions of Venus were entirely from the heated gases, carried across the surface by convection, then it should be composed of emission bands of CO_2 at 4.3μ, 10.0μ and 14.5μ and ozone at 10.5μ. The emission bands of CO_2 would be greatly depleted in intensity in passing through the earth's atmosphere. Assuming that the earth's atmospheric ozone is greatly reduced in the night time, only the ozone emission band at 10.5μ, emanating from the atmosphere of Venus, would be transmitted, with any degree of intensity, to the radiometric instruments.

Apparently, it is necessary to admit that some of the observed planetary radiation emanates from the surface of Venus; although the large ratio of the spectral components ($A \div B = 2$) indicates a possible selective emission of CO_2 and ozone at 10.5μ. If the rotation period is long (225 days) then it seems necessary to assume that the interior of Venus still has internal heat to maintain the surface at a comfortably warm temperature. While this assumption may be novel, it seems as plausible as to assume that the dark surface is kept warm by conduction from heated atmospheric gases convected 1000 miles or more over the surface from the irradiated regions of the planet.

The higher temperature condition in the southern hemisphere may be seasonal. For the galvanometer deflection caused by the radiation (sunlight) from the southern hemisphere (cusp) in its passage through the water-cell, was larger ($4 \div 3$) than from the northern hemisphere. This would indicate greater cloudiness (and a higher albedo) which would occur in the summer season. A photometric study of the surface of Venus should prove profitable in establishing the condition of brightness in these two hemispheres, to determine whether or not there is a real difference in brightness, and whether it is seasonal. From this it appears that the photometric and the radiometric measurements may yet prove to be a means of determining the position of the axis of rotation of Venus.

4. MARS.

Under the present caption are given various details concerning the radiation measurements on Mars. Those relating to special measurements in order to obtain an answer to certain specific questions are given in a subsequent part of this paper.

The first series of this year's measurements were made with a thermocouple (No. 13–2) which intercepted the whole planetary image. The second group of measurements was made with the U-shaped thermocouple No. 12–1, which intercepted about 0.49 of the diameter of the disc of the planet. Owing to the peculiar construction of, and the manner of observing with, this thermocouple, it was possible to attain a very high accuracy, as described in a previous paper.[46]

The observations of 1922 on the north and south hemispheres were repeated and verified. Moreover, new observations on the

[46] *B. S. Sci. Papers* (No. 360), 18, p. 544, 1922.

east and west limbs showed that the morning, or sunrise, side of the planet is much cooler than the afternoon side of Mars. (Table V.)

These data were obtained at the 18.4-ft. focus and were, of course, preliminary to the final efforts, using a still smaller receiver at the 53.3-ft. focus, in which it was possible to practically isolate the polar caps and other well-defined areas.

Atmospheric conditions remained remarkably steady when observing on the central part of the disc. For example, on August 1st, from 2:12 to 3:12 A.M., while observing the radiation from the dark area called Syrtis Major, the average "no cell" deflection was 166 mm. at the beginning, and 168 mm. at the conclusion, one hour later; while one intermediate series gave an average deflection of 170 mm.

Further data on isolated areas are given in Table V, while in Table VI are assembled all the data relating to the spectral components of the planetary radiation emanating from Mars. The humidity data given in the last column of Table VI are of general interest in showing atmospheric conditions at the surface of the earth. Frequently the transmission data fluctuate with the humidity, especially for the fluorite screen. This is owing to the great effect exerted by moisture upon the long wave-lengths. Frequently, however, the values of the transmissions are not in accordance with the observed humidities. From this it appears that the humidity measurement at the surface is not always an accurate test of atmospheric conditions as regards the total content of water vapor in the atmosphere.

It may be noted when the humidity was high, hence causing an increased absorption of the long wave-lengths, usually all the screens show an increase in transmission.

These measurements are a part of a series that should be made when Mars is nearest and also farthest from the Sun, in order to determine the water-cell transmissions and the temperature with variation in distance.

It is relevant to record that the Lowell Observatory is situated in a region in which the months of July and August are known as the "rainy season." Fortunately during the present season weather conditions were quite unprecedented. For ten days preceding the maximum brilliancy of Mars there was no rain, the humidity was unusually low and the nights were cloudless. This

condition continued until early in the morning of August 23rd, when check measurements on the Moon were interrupted by fleeting clouds.

5. JUPITER.

The mean value of the water-cell transmissions obtained in 1922 was 68.2 per cent., indicating that the planetary radiation from Jupiter is very small. For those measurements a receiver was used which intercepted about one-fourth of the diameter of the image of the planet. After making a correction for the zero shift of the galvanometer reading on opening and closing the shutter, the same results were obtained when using an opaque cardboard shutter before the thermocouples as when the observations were made by exposing the receivers alternately to the sky and the planetary disc, which is the usual method of making the measurements.

In the present measurements thermocouple No. 2 in the vacuum container No. 13 was used. The receiver intercepted about one-half of the image of the planet. In view of the fact that there is but little planetary radiation, it is immaterial whether the radiometer window is of fluorite (1922) or rock salt.

The observations were made when the planet was on the meridian, the aqueous pressure being less than 0.5 cm. The measurements were made by exposing one receiver alternately to the planetary disc and to the sky; the receiver intercepting about one-half of the image of the disc. A set of measurements consisted of a series of galvanometer readings (1) without the water-cell or other screen interposed, then a series of readings (2) with the water-cell interposed in the path of the incoming radiation followed by a series of readings (3) without the water-cell. The mean value of (2) divided by the mean value of (1) plus (3) gives the water-cell transmission. Two such sets of measurements gave an average (of 65.9 and 68.0 per cent., respectively) value of 67.0 per cent., or 72.8 per cent. when corrected for losses by reflection from the surfaces of the cell. This value is practically the mean (Table I) of the observations of 1914 and of 1922 and indicates that while there is some planetary radiation, from Jupiter, of wave-lengths transmitted by our atmosphere, it is very small. This was further verified by means of the thin glass screen which excludes only the planetary radiation, extending from 8 to 15μ and amounting to 3.7 per cent. The measure-

ments of August 16th, using the 53.3-ft. focus, gave an average transmission of 74.8 per cent., which is close to the transmission of solar radiation, –75.5 per cent.

The measurements of 1922 seem to indicate that the water-cell transmission of the radiation from the dark bands of Jupiter is less (the planetary radiation is greater) than from the bright bands. The recent measurements of Pettit and Nicholson [47] also show a lower (about 2 per cent. lower) water-cell transmission of the radiation from the dark bands than from the bright areas of Jupiter. This is probably to be expected on the basis that the dark areas absorb more solar radiation and, hence, become more highly heated than the bright areas. In view of the fact that these dark areas are continually changing, this seems to be an interesting subject for prolonged systematic investigation.

In the paper by Pettit and Nicholson [48] attention is called to the fact that their water-cell transmissions of the radiation from Jupiter and from Saturn, in the spectral region of 0.3 to 1.4μ, are higher than that of the Sun. This is at variance with all of our measurements, past and present, although they used apparatus which is practically identical with our own. There are so many sources of difficulties in making these observations that this discrepancy is probably to be sought for in temporary changes in the apparatus and in terrestrial atmospheric conditions, rather than in temporary changes in the (selective) emission, absorption and reflection of the atmospheres of these two planets at the time when they made their observations.

The observational data on Jupiter are given in Table III. The ratio of the components of planetary radiation (at 8–15μ) indicates such an absurdly high temperature that no credence can be given to the result. The quantities measured are extremely small, and this inconsistency in the estimated temperature is no doubt ascribable (1) to a combination of errors of observation, (2) the selective emission, absorption and reflection of the atmosphere of Jupiter, and (3) the presence of reflected solar radiation.

In view of the fact that the southern hemisphere of Mars and of Venus (the south cusp and adjacent dark region) were found to be hotter than the northern hemisphere, an examination was

[47] PETTIT and NICHOLSON: *Publ. Astronom. Soc. Pacific*, **35**, p. 196, 1923.
[48] PETTIT and NICHOLSON: *Pop. Astron.*, **32**, p. 76, 1923.

made (September 11th, 7:45 P.M.) of the north and south polar regions of Jupiter, at the 53.3-ft. focus. Both the direct deflections and the water-cell transmissions showed no difference in the radiation and, by inference, in the temperature of the polar regions of Jupiter.

6. SATURN.

The observations were made early in the evening (9 to 10 P.M.) when the planet was on the meridian. The radiometer was thermocouple No. 2 in vacuum container No. 13. The receiver intercepted the whole of the ball of the planet; thus differing from the measurements of 1922, in which the receiver covered about one-half of the central disc.

On June 20th, three series of water-cell transmissions (61.2, 62.7 and 60.8 per cent., respectively; uncorrected for reflection) gave a mean value of 61.6 per cent. On June 21st, conditions were unusually steady so that during the course of the observations, which occupied about one-half hour, the galvanometer deflection (mean value deflection = 0.56 cm. at 9:15 P.M., and = 0.58 cm. at 9:40 P.M.) remained constant to within 2 per cent. On this evening two series of water-cell transmissions (61.6 and 64.2 per cent., respectively) gave a mean value of 62.9 per cent. The mean value of the water-cell transmissions for the two evenings is 62.3 per cent., which is close to the value obtained in 1922; and it is appreciably lower than the water-cell transmissions of the radiation from Jupiter, as observed on previous years. These measurements indicate an appreciable amount of planetary radiation from the ball of Saturn.

Interspersed with these measurements of the radiation transmitted through the water-cell were similar measurements of the radiation transmitted through the glass screen and also through the fluorite screen. These screens are also consistent in showing appreciable planetary radiation emanating from the ball of Saturn.

No accurate indications could be obtained of the radiation from the rings of Saturn this year. The statement in the previous paper [49] that in 1922 the rings of Saturn were too narrow and of too low intensity to measure radiometrically is incorrect. As a matter of fact, two series of water-cell transmissions (60.0 and 60.4 per cent., respectively; mean value 60.2 per cent.) were obtained on the ball of the planet, and one series of transmission

[49] *B. S. Sci. Papers* (No. 460), 18, p. 547, 1923.

measurements (giving a value of 64.5 per cent.) was made on the rings. The above-mentioned reference should therefore have stated that owing to the low intensity and narrowness of the rings of Saturn the radiometric measurements could not be made with high accuracy. This was one reason for not tabulating the data. However, a further examination of the data, in connection with this year's measurements, shows that the errors of observation on the rings were not greater than obtained in the measurements on the disc of the planet. Moreover, the deflections observed through the water-cell were consistently higher for the rings than for the disc.

The close coincidence of the numerical values of the transmission of the radiation from the ball and from the rings, as well as the significance of the results, were not noticed at the time. At this late date it is impossible to know whether, in setting the receiver on the rings, any radiation from the ball was also intercepted. The low value of the transmission from the rings of Saturn would indicate the emission of a small amount of planetary radiation, although less than from the ball of the planet.

As already stated, the details of construction of the thermocouples, as well as the methods of operation, used by Pettit and Nicholson [50] are essentially the same as our own, and in general there is a close agreement in the results obtained, as is to be expected. However, in the case of Saturn there is an outstanding difference in the water-cell transmission measurements, and in the interpretation of the results.

First of all their water-cell transmission percentages of the radiation from Jupiter and from Saturn [51] are higher than that of the direct solar radiation, when the reverse would be expected.

There are several difficulties involved in making these measurements: (1) The change in focus, and difficulties in focussing, when the water-cell is interposed and (2) the planetary measurements are made at night while the solar radiation measurements are made in the daytime when atmospheric conditions of humidity, dust and smoke are presumably different, especially at the lower elevation. Our measurements for 1914 (a rather low value, owing perhaps to poor focussing), 1922 and 1924 are consistent

[50] PETTIT and NICHOLSON: *Astrophys. Jour.*, **56**, p. 295, 1922. COBLENTZ: *B. S. Bull.* (Nos. 229 and 244), 11, pp. 131 and 613, 1914.

[51] PETTIT and NICHOLSON: *Publ. Astronom. Soc. Pacific*, **35**, p. 196, 1923.

in giving a lower water-cell transmission (higher planetary radiation) for Saturn than for Jupiter. Moreover, these measurements are lower than similar water-cell transmission measurements of the direct solar rays.

An interesting result obtained by Pettit and Nicholson is that the glass-screen transmissions indicate only about one-fifth as much planetary radiation from the rings as from the disc of Saturn. They have interpreted their data [52] as indicating that the radiation from Saturn's rings is practically all reflected sunlight. This, of course, is not an unreasonable conclusion, and might be expected in view of the great solar distance. Their observed spectral component of the planetary heat from the disc of Saturn is 7.9 per cent. as compared with our value of 12.2 per cent. The lower value at the lower elevation is to be expected.

Based upon their observations of the planetary radiation (1.5 per cent.) from the rings our value would be about 2.3 per cent., which is comparable with our value obtained in 1922.

The interpretation of our data would be that both the ball and the rings of Saturn emit a small amount of planetary radiation. This, of course, might be true even though the rings (without an atmosphere) radiated like the Moon, whereas the ball might emit radiation as a result of a possible high internal temperature.

In view of the above-mentioned discrepancies, especially as regards the planetary radiation emitted by the rings of Saturn, a further and prolonged study should be made of this question.

The observational data on Saturn are given in Table III. The numerical value of the ratio of the components of the planetary radiation at 8 to 15μ is close to 3. This indicates an extraordinarily high temperature. Since the quantities of planetary radiation measured are extremely small, the presence of reflected solar radiation will complicate the evaluation. Hence, for the present, no attempt will be made to determine the source of this inconsistency which has already been noticed in similar measurements on Jupiter.

7. URANUS.

The physical condition of Uranus is practically unknown. Its atmosphere is probably similar to that of Jupiter and Saturn with dark and bright areas, which would account for the observed fluctuations in brightness, observed photometrically.

[52] PETTIT and NICHOLSON: *Pop. Astron.*, **32**, p. 76, 1923.

On the nights of June 27th and 28th, some interesting observations were made on the planet Uranus, using thermocouple No. 2 in mounting No. 12. The planet was on the meridian and the double-throw deflection was 3.0 and 2.8 mm., respectively, on these two dates. Owing to unsteadiness of the galvanometer reading no accurate measurements were obtained of the radiation transmitted by the water-cell. The deflections, however, were appreciable, indicating that if any planetary radiation is emitted it is small in amount.

A further examination was made on September 14th, using thermocouple No. 2 in vacuum mounting No. 11. The galvanometer (single) deflections ranged from 2.0 to 2.5 mm. The transmission through the glass screen was within 8 to 10 per cent. the same as the direct deflection, showing that if planetary radiation of wave-lengths greater than 8μ is emitted from Uranus, it is small. The transmissions observed through the water-cell ranged from 65 to 75 per cent., with an average of over 70 per cent., showing that (within the large experimental errors) the observed radiation is practically all of solar origin. This is probably to be expected in view of the great solar distance, which would prevent heating of the atmosphere. For even though the planet is still hot, the atmosphere might be so dense and so filled with water vapor that infra-red radiation would be completely intercepted.

8. THE MOON.

An excellent series of radiometric measurements was obtained on the Moon, about 4:30 A.M., on June 24th, using thermocouple receiver No. 2, in vacuum mounting No. 13. The Moon was then in its last quarter, age twenty-two days. The measurements were made on the brightest area situated midway between Grimaldi crater and the eastern limb of the Moon. The spectral components are given in Table IV, the aqueous pressure being about 0.5 cm. An interesting feature of these measurements is the equality of the spectral components (amounting to 37.8 per cent.) of the planetary radiation extending from 8 to 12.5μ and 12.5 to 15μ. On this same morning a ratio of 3 to 4 (18.4 to 24.6 per cent.) was observed in the spectral components of the planetary radiation from Mars, using a receiver which intercepted the whole image of the planet.

An interesting series of observations was obtained on the Moon on August 6th, 8 P.M. The age of the Moon was six days, and the measurements were made close to the edge of the west limb, midway between the horns. The humidity was low.

The ratio of the spectral components of the planetary radiation at 8–12.5μ and 12.5–15μ is 2 : 3. The calculated black-body temperature required to give this ratio is 400° K., or about 125° C. Quite similar results were obtained on August 15th (Moon fifteen days old), using a 40-ft. focus, and a receiver 0.23 mm. in diameter, repeating the measurements of June 24th on a bright area a short distance below the Grimaldi crater and the eastern edge of the Moon. The gradual change in the ratios of the spectral components with change in phase and increase in temperatus is instructive.

In view of the aforementioned question whether the excess radiation is from the planet to the thermocouple receiver or from the receiver to the planet, a further series of measurements was made (4 A.M., July 22nd, and again at 8 P.M. on August 6th) on the unilluminated parts of the Moon.

The method of observing was the usual one in which both receivers are exposed to the sky; then one receiver is exposed alternately to the sky and to the dark area (in the cusp, near the north and south poles) of the Moon.

Under the same conditions that an exposure of the receiver to the bright part of the Moon threw the galvanometer deflection off the scale (50 cm.), the unilluminated areas did not indicate a deflection as great as 0.1 cm. On the other hand, setting the receiver on a small bright peak in the dark part of the lunar disc caused a deflection of about 0.8 cm.

The information disclosed by this series of measurements is that the unilluminated lunar surface cools rapidly to a temperature (and emissivity) which is close to that of the effective radiating layer of the earth's atmosphere. From this it is evident that the temperature of the irradiated surface, especially of the Moon and of Mars, rises considerably above that of the effective radiating layer of the earth's atmosphere, although further data, of a different nature, are required to show whether or not the temperature of the planet is higher than that of the radiometer receiver.

TABLE IV.

Spectral Components in Per Cent. of the Total Radiation from the Moon.

The Total Radiation of All Wave-lengths between 0.3 and 15μ Is Taken 100 Per Cent.

Date, 1924. M.S.T.	Moon's Age (days).	Thermo-couple.	Observed Spectral Components.				Solar and Planetary.		Planetary.			Ratio *A*:*B*.	Temperature.	Press Aqueous Vapor.
			Fluorite λ0.3 to 12.5μ	Glass λ0.3 to 8μ	Quartz λ0.3 to 4.1μ	Solar. Water λ0.3 to 1.4μ	λ1.4 to 4.1μ	λ4.1 to 8μ	λ1.4 to 8μ	λ8 to 12.5μ *A*	λ12.5 to 15μ *B*		°C.	cm.
June 24, 4:30 A.M.	21.9	No. 13–2	62.2	24.4	22.1	12.6	9.5	2.3	7.7	37.8	37.8	100	140	.48
August 6, 8:20 P.M.	6.3	No. 13–2	52.3	20.6	18.0	10.1*	7.9	2.6	8.3	31.7	47.7	67	70	.30
August 15, 12:45 A.M.	14.5	No. 11–2	66.4	42.5	39.6	24.1	14.5	2.9	9.6	23.9	33.6	71	80	.54
August 18, 3:10 A.M.	17.6	No. 11–2	64.7	30.5	28.4	17.1	11.5	2.1	8.1	34.2	35.3	97	150	.39
August 20, 2:15 A.M.	19.7	No. 11–2	66.2	29.5	27.6	15.5	12.1	1.9	9.0	36.7	34.8	106	155	.30
August 25, 4:45 A.M.	24.8	No. 11–2	57.0	28.6	....	15.8*	....	...	7.7	28.4	43.0	66	60	.52
September 12, 12:30 A.M.	13.0	No. 11–2	66.2	34.3	....	17.4	....	...	11.3	31.9	33.8	94	125	.64

*Poor series.

The observations of June 24th are interesting in showing a practically pure planetary radiation of 75.6 per cent. of wave-lengths 8 to 15μ. In the region of 1.4 to 8μ the spectral component radiation is 11.8 per cent. as compared with 12.6 per cent. for the region of 0.3 to 1.4μ. As already mentioned, the corresponding components of solar radiation are 24.3 per cent. and 75.5 per cent. (ratio = 0.322), respectively. From this it follows that the planetary radiation of wave-lengths 1.4 to 8μ is [11.8 4.1(= 12.6 × 0.322)=] 7.7 per cent. This is practically 5 per cent. of the total lunar planetary radiation previously observed with the water-cell, and demonstrates the propriety of having used the water-cell in our measurements of 1922.

A good example of the rapid increase in temperature with time of insolation is found in the measurements of August 18th and 20th, on the brightly illuminated region half-way between the Riccioli crater and the limb of the Moon.

The water-cell transmissions observed through the glass window, which screens out the planetary radiation, were found to remain practically constant, whereas the transmission observed through the rock-salt window decreased from 17.1 to 15.5 per cent. (Table IV), which is explainable on the basis of two days' additional insolation.

The various observational data on the Moon are tabulated in Table IV. All the data are corrected for reflection losses (8.5 per cent.) from the screens, but not for absorption by the silvered mirrors. The indicated time of the observations is half-way between the beginning and the ending of the series, which required twenty to forty minutes.

The first two series using thermocouple No. 2, in the vacuum mounting No. 13, were made at the 18.4-ft. focus, using the diagonal mirror. The subsequent series were made with thermocouple No. 2 (diameter of receiver 0.23 mm.) in the vacuum mounting No. 11, at the 53.3-ft. focus, using an additional convex mirror.

The observations of August 6th were made by placing the receiver closely tangent to the limb, half-way between the cusps. Most of the observations were made on the afternoon side of the Moon when it was close to Mars, and close to the meridian, in order to obtain comparative results.

The measurements of June 22nd were made by setting the thermocouple receiver midway between the Grimaldi crater and the eastern limb of the Moon.

It is relevant to call attention to the difficulty of making consistent radiometric measurements on the Moon when using an enlarged image (53.3-ft. focus) and a small (0.23-mm. diameter) receiver owing to great difference in brightness of the lunar surface. Selecting an isolated bright area which was but little larger than the receiver (see data of August 18th), a slight displacement into the surrounding dark area decreased the deflection by 10 to 20 per cent. Whereas, by setting the receiver accurately on the bright spot, the readings were in agreement to within 2 per cent. Hence, the measurements of August 15th, 18th and 20th were made on the evenly illuminated area half-way between the Riccioli crater and the limb, as already described.

The application of these data as a calibration of the temperature of Mars may be found in a subsequent part of this paper. In this connection it is of interest to notice the change in magnitude of the ratio of the spectral components, 8 to 12.5μ and 12.5 to 15μ, with an increase in insolation and, hence, temperature of the afternoon side of the Moon.

9. RADIATION FROM TERRESTRIAL SOURCES.

The chief difficulty in obtaining accurate measurements of planetary radiation is in eliminating, or correcting for, the exchange of radiation from the radiometer receiver to the object.

Fortunately in the measurement of the radiation from celestial objects the sky can be used as the shutter, and the telescope can be tilted so as to cause the thermocouple receivers to intercept the incoming radiation from the star or planet under investigation.

The measurement of the radiation from some terrestrial object, such as, for example, a distant mountain peak, or the roof of a building, involves greater difficulties, owing to the extended areas which will be projected upon the two receivers, if one were to proceed as in the measurement of celestial objects.

On first consideration it was planned to use two thermopiles, connected in series so as to act as a single thermocouple, with circular receivers.[53]

[53] *B. S. Bull.* (No. 229), 11, p. 131, 1914.

Each receiver was to be at the focus of a reflecting mirror of about 1 cm. focal length and 10 to 15 cm. in diameter. These mirrors and thermopiles were to be mounted side by side and enclosed in long narrow tubes to reduce the size of the object to be focussed upon the receiver. The proposed method of operation was to keep the sky projected upon one receiver, and by tilting its accompanying mirror the other receiver was to be exposed alternately to the sky and to the terrestrial object.

In actual practice it proved inexpedient to perform the experiments in this manner at this time. Instead of the above-mentioned balanced radiometer, a single thermopile with a circular receiver 4 mm. in diameter was mounted at the focus of a silvered glass mirror 15 cm. in diameter and 60 cm. in focal length. This mirror was mounted upon a horizontal axis and (using suitable stops) could be tilted so as to project alternately the sky and the terrestrial object, *e.g.*, a roof or a distant mountain peak, upon the thermopile receiver. Or, by keeping the mirror stationary and using a black cardboard shutter directly in front of the thermopile, galvanometer readings could be obtained of the radiation to or from the sky and from the terrestrial object. Usually the measurements of the radiation from terrestrial objects, by these two methods, were in agreement.

Observations made in the daytime on the sky, on the horizon, and, hence, on a large air-mass, gave a positive deflection. On tilting the mirror so as to project an image of the cloudless sky, somewhat above the horizon, upon the thermopile receiver, and opening the shutter indicated no incoming radiation. By tilting the mirror still more so as to still further decrease the air-mass, and opening the shutter, the galvanometer gave a negative deflection indicating outgoing radiation from the thermopile.

The water-cell always seemed to have a different temperature from that of the shutter. Hence, in order to maintain a stationary zero reading of the galvanometer, when the water-cell was used it was placed directly in front of the thermopile and the cardboard shutter was placed between the water-cell and the mirror.

While the measurements of the heat radiated from terrestrial objects is instructive in connection with the foregoing measurements of planetary radiation, they can not be exact duplicates of the latter because of the limited extent of the air-path traversed,

and hence the incompleteness of the absorption in certain spectral regions. Nevertheless they assist in clarifying our ideas on the subject.

The actual numerical values may not be entirely free from observational errors. But the whole question involves only approximate values, in view of the lack of information regarding heat lost by air-convection, by conduction in the materials studied, etc. It is a common observation that stone walls, brick buildings, etc., continue to emit radiation for some time after sunset. On the other hand, the surface of a pile of sand cools quickly, while the layers underneath continue to be perceptibly heated. In the course of the present observations on a concrete driveway it was remarkable how quickly the emitted radiation decreased in intensity with each passing cloud, only to return to its normal value after the cloud had passed.

(*a*) *Measurements at Washington, D. C.*—The difficulties encountered in making measurements at this station (close to sea-level) were mainly owing to the ever-changing clouds, which prohibited using the sky as a shutter, and also caused great variations in insolation of the various objects studied; for example, tops of trees, grass, a concrete driveway (sometimes covered with kaolin or sand), buildings, etc.

The measurements were made by observing through an open window of the radiometric laboratory of the Bureau of Standards which is on the ground floor of what is known as the "South" building.

An interesting object, giving trustworthy radiometric measurements, was the Electrical Building situated about 100 metres directly east of, and at a somewhat lower level than, the observing station. The walls of the lower story, and the trimmings of this building are of fine-grained (Indiana) limestone, while the remaining three stories are of vitreous-coated red brick. The roof, which extends NS., is of corrugated red tile.

A series of observations, made on May 26th, which was an unusually clear day (solar radiation intensity $Q = 1$ to 1.2 gr. cal. per cm.^{2} per min.), are worthy of permanent record. In the forenoon, as the insolation and consequent heating increased, the water-cell transmissions of the radiations from the roof decreased from 35 per cent. at 11 A.M. to 24 per cent. at 12 N., which decrease is to be expected. At 1:30 P.M., when the insolation was

practically vertical incidence to the roof, the water-cell transmission was only 14.7 per cent., which reminds one of similar values (but of different spectral quality) for the Moon.

At 3:30 P.M., after insolation for several hours (the solar rays being incident at about 30° at that time), the water-cell transmission of the radiation emanating perpendicularly from the red-brick walls was 43 per cent. while that from the horizontally adjoining grayish-white limestone was 58 per cent. In comparison with this, the water-cell transmission of the direct solar radiation is about 70 per cent.

The ratio of the intensities (6.6 and 12.8 cm., respectively) of the radiation emanating from these two materials and transmitted by the water-cell is a rough measure of their diffuse reflection or relative brightness. This ratio is 0.51. In other words, the reflecting power of this limestone is twice as great as that of the red bricks. This, as is to be expected, has a marked effect upon the ("planetary") heat radiation emanating from these two substances. The red-brick wall, which absorbs twice as much solar radiation, emitted more than twice as much planetary radiation as the lighter-colored limestone—the calculated values of the planetary radiation being, respectively, 39 and 17 per cent. These measurements are interesting in that, in a general way, they are directly applicable to the foregoing questions of the heating of the planets by solar radiation, and their consequent emission of planetary radiation.

(*b*) *Measurements at Flagstaff, Ariz.*—The measurements were made from the north porch of the library building of the Lowell Observatory (elevation, 7250 feet). To the north are the San Francisco mountains. The measurements were made on the southern slope of Mt. Agassiz, which is at a distance of about 9 miles (15 km.) and has an elevation of over 12,300 feet. The peak, which is somewhat pyramidal in form, and the upper part of the slope of this mountain consist of bare andesite rock. Further down the slope is a more level meadow, covered with grass; and directly below this grass-covered slope is a similar area covered with pine trees. The mesa intervening between this mountain and the observing station is sparsely covered with a pine forest.

Radiometric measurements were made on these three well-defined spots; the observations on the bare rocks being made

somewhat to the right of the sharp ridge, in the hollowed-out portion of the saddle, which leads to an adjoining peak of lower elevation.

The measurements were made during the middle of the day, in the latter part of June (17th to 25th), when the solar radiation was incident practically normal to the mountain slope. The sky being cloudless, a prolonged series of measurements could be made either (1) by tilting the mirror and using the sky directly above the peak as a shutter, or (2) by keeping the mirror stationary and focussing the sky or object upon the thermopile receiver and using a cardboard shutter, as already described. The latter method gives a measure of the incoming sky radiation or outgoing nocturnal radiation. By applying this correction the radiometric measurements obtained by these two methods were usually found in excellent agreement. However, on account of the closeness of the optical path above the tree tops, in some of the measurements close to the horizon there is evidence of atmospheric radiation from the intervening air-path. This seems to be the explanation for some inconsistent results obtained on a low-lying volcanic cone (Turkey Hill) situated some twelve miles to the east, and practically on the horizon, of the observing station.

The water-cell transmission of the radiation emanating from the bare rocks near the mountain peaks was 57.3 per cent. at noon on June 19th, which is equivalent to a planetary radiation of over 17 per cent. On June 25th at 1:45 P.M. (M.S.T.) when the solar rays were not incident so favorably upon this part of the peak, the water-cell transmission was 63 per cent., or equivalent to a planetary radiation of about 9 per cent. The bare rocks and the pine forest reflected practically the same amount (galvanic deflection 7.6 and 9.0 cm., respectively, through the water-cell) upon the thermocouple receiver.

Similar observations were made (2 P.M., July 25th) on the grassy slope, the equivalent planetary radiation (water-cell transmission, 69 per cent.) being only about 1 per cent. This low value is partly owing to the fact that this spot reflected the solar radiation much more highly (galvanic deflection 12.1 as compared with 7.6 cm. for the rocks) than the bare rocks, or the pine forest. Another reason for obtaining a low planetary radiation, as shown in a previous paper,[54] is that the temperature of growing vegeta-

[54] *B. S. Sci. Papers* (No. 460), 18, p. 547, 1923.

tion is but little higher than that of the surrounding air and, hence, cannot emit much radiation.

The two sets of measurements (without the water-cell) of the radiation from the pine forest were somewhat inconsistent, which, as already explained, was no doubt owing to the fact that the optical path was close above the trees on the intervening mesa. However, the data show that the planetary radiation emitted was small.

The foregoing results were a little surprising, at first, in view of the high elevation and clear sky. But when one considers the loss of heat by air-convection and the greater facility for radiating into space (nocturnal radiation), it is not so surprising to find a low emission of planetary radiation from objects at these high elevations. It was a common experience on the tree-covered (mesa) observatory grounds to find light-colored rocks (*e.g.*, granite) only perceptibly warmed, while the darkest rocks and loose sand became comfortably heated by the sun. On the other hand, a low-lying unpainted tin roof became burning hot to the touch, which is easily explained in view of its high absorptivity of the incoming solar rays and its low emissivity for the outgoing, long wave-length infra-red rays.

Turning from the tree-covered areas to the wide expanses of desert country, where the vegetation is low-growing and sparse, it was found that the surface and the closely overlying strata of air became very noticeably heated by the sun.

The results of these measurements on terrestrial objects is instructive in connection with the question of the probable rise in temperature of, and the planetary radiation from, the surfaces of the planets. The temperature rise of some of these objects studied was from 5 to 15° above the surrounding atmosphere.

These measurements are to be considered preliminary to what is hoped to be a more elaborate and a more thorough-going investigation of this subject, in which more consideration is given to wind velocity, the intensity and duration of the insolation, as well as the resulting rise in temperature.

IV. DISCUSSION OF THE DATA AND TEMPERATURES ON MARS.

The main problem in this year's program was the measurement of the radiation of Mars. Under the present caption are given data which pertain to the special questions investigated.

TABLE V.

Water-cell Transmissions in Per Cent. of the Total Radiation Emanating from, and Temperatures of, Isolated Regions on Mars. The temperatures are subject to slight revision in the final publication in the Lowell Observatory Bulletin.

Date, 1924. M.S.T.	Thermo-couple.	East Limb (morning).	Equator; Centre of Disc.	West Limb (afternoon).	North Polar Region.	South Polar Region.	Remarks.
			18.4-foot Focal Length.				
July 30	No. 12–1	41.4	37.2	....	42.5	37.6	Receiver intercepts about 0.49 of disc image of Mars.
August 1	No. 12–1	42.3	37.0	37.0	48.2	39.5	
August 2	No. 12–1	42.2	39.1	38.5	44.2	38.8	Poor series; humidity varied.
August 6	No. 12–1	39.0	32.8	35.8	....	....	Syrtis Major in centre of disc. East and west limbs seem equally illuminated.
September 13	No. 11–21	38.2	25.1	25.3	33.6	26.4	Good seeing, Syrtis on east limb. Receiver = 0.35 of disc.
September 14	No. 11–21	....	29.3	....	42.3	29.2	Mare Cimmerium.
			53.3-foot Focal Length.				
August 13	No. 11–21	47.8 − 33° C.	32.0 12° C.	34.4 6° C.	74.4 − 70° C.	72.6 − 68° C.	Receiver covers about 0.11 of disc.
August 14	No. 11–21	52.0 − 41° C.	30.8 16° C.	35.5 3° C.	74.1 − 70° C.	72.0 − 67° C.	South polar cap is covered by receiver.
August 15	No. 11–21	54.2 − 45° C.	32.4 10° C.	36.4 0° C.	....	....	Mare Sirenum on central meridian, extends dark to east limb. West limb bright.
Do	No. 11–21	....	36.3 0° C.	....	....	....	Light colored region on meridian adjoining Mare Sirenum on north.

August 17	No. 11–21	....	34.5 7° C.	....	....	....	Light colored region on meridian adjoining Mare Sirenum on north.
Do	No. 11–21	....	28.4 30° C.	....	77.4 − 72° C.	75.2 − 70° C.	Mare Sirenum is 0.85 as bright as adjoining lighter colored area and emits 6 per cent. more planetary radiation.
August 21	No. 11–21	....	34.9 6° C.	....	....	....	Light colored region, same as above.
Do	No. 11–21	....	32.5 14° C.	....	79.0 − 75° C.	71.6 − 70° C.	Poor seeing; Mare Sirenum on central meridian.
August 23	No. 11–21	55.8 − 47° C.	32.8 22° C.	35.6 3° C.	73.4 − 69° C.	69.5 − 64° C.	Light colored region central on meridian.
August 28	No. 11–21	....	31.2 21° C.	....	75.1 − 70° C.	70.6 − 66° C.	Solis Lacus on meridian. Poor seeing.
September 11	No. 11–21	66.3 − 60° C.	30.8 22° C.	36.4 0° C.	72.5 − 70° C.	62.5 − 56° C.	Syrtis Major on meridian.
September 12	No. 11–21	66.1 −60°C.	32.4 15° C.	33.6 10° C.	69.3 − 65° C.	54.5 − 42° C.	Syrtis Major, central.

September 12	No. 11–21	47.7 − 33° C.	....	....	....	Half-way between centre and east limb.
Do	No. 11–21	....	37.8 − 5° C.	....	....	Half-way between centre and west limb.
Do	No. 11–21	....	....	49.7 − 35° C.	....	Half-way between centre and north pole.
Do	No. 11–21	....	....	....	40.3 − 16° C.	Half-way between centre and south pole.

1. RADIATION FROM AND TEMPERATURES OF SELECTED REGIONS.

Under this caption it will be shown that, when observed on the central meridian, hence under the same illumination and air-mass, the dark areas on Mars emit a greater amount of planetary radiation, and are no doubt hotter than the bright areas. From this it seems evident that it would be futile to attempt a zonal radiometric survey of the whole surface unless a complete specification can be made of the conditions under which the observations are made.

The present measurements were, therefore, made on selected regions, using a radiometer receiver that was practically the same size as, or smaller than, the areas studied. The data are given in Tables V and VI, to which reference may be made in connection with the following discussion of the results of these measurements.

(*a*) *Bright and Dark Regions.*—Whether the measurements were made with a receiver covering 0.4 or 0.11 the diameter of the image of the planetary disc, the data are in agreement in showing a lower water-cell transmission, and, hence, a higher planetary radiation from the dark regions than from the bright regions.

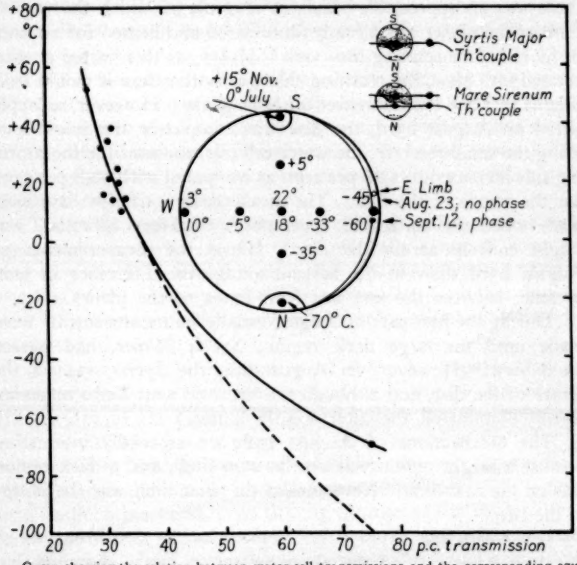
An exceptionally good opportunity for testing the difference in the planetary radiation emanating from equally illuminated bright and adjoining dark regions was obtained on August 15th and 17th. The particular parts on the meridian were the dark area, known as *Mare Sirenum,* and the bright region directly to the north (see rough sketch in Fig. 2). The measurements of August 21st were made nearer to the point of this dark area, known as the " Beak of the Sirens."

In all cases the dark regions have a lower water-cell transmission than the bright areas. These water-cell transmissions are proportional to the albedo. Hence, the ratio of the galvanometer deflections observed on the dark region, *Mare Sirenum,* relative to the adjoining bright area, shows that on August 17th (11 : 45 to 12 P.M.) the ratio of brightness was (32 : 38 =) 0.85. In other words, as a result of a 15 per cent. greater absorption, the dark area emitted about 6 per cent. more planetary radiation.

This is somewhat at variance with the data given elsewhere in this paper (terrestrial sources) where a light-colored limestone wall appeared twice as bright as the adjoining dark brick, and emitted only half as much low-temperature radiation. In this respect the data of August 21st are in better agreement. At this

time the difference in brightness, as measured by the deflection through the water-cell, appeared to be about 4 to 5 per cent., and the darker area emitted 7.5 per cent. more planetary radiation. For the latter series the seeing was rather poor. However, in all cases more planetary radiation was emitted from the dark regions

FIG. 2.



Curve showing the relation between water-cell transmissions and the corresponding equatorial temperatures on Mars; also temperatures on different parts of the surface and positions of thermocouple receivers on the disc of Mars.

than from the bright ones. As will be shown presently, in the discussion of planetary temperatures, from visual and photographic observation, it has been evident that these dark areas cannot be bodies of water.

(*b*) *East and West Limbs.*—All the measurements, with the large and the small receivers, are in agreement in showing that the east limb, which is the side just turning into the sunlight, has a higher water-cell transmission than the west limb. In other

words, the sunrise side of the planet is cooler than the side under the afternoon sun. The west or afternoon side of the planet is really hotter than indicated; but owing to the larger air-mass than on the central meridian the intensity of the planetary radiation is reduced.

During the latter part of July and the first part of August, there was an appreciable phase, as a result of which the eastern limb of the planet was already illuminated and heated for an hour or more before rotating into view. Hence, as this heated portion rotated into view, the morning side was hotter than it would have been if this had been observed without phase. However, at opposition on August 23rd, the disc was completely irradiated and, using the small receiver, the water-cell transmission for the morning side increased to 55.8 per cent. as compared with 32.8 per cent. for the centre of the disc. The measurements of this date were made when the equatorial zone, north of *Mare Sirenum*, was bright entirely across the disc. Hence the measurements of August 23rd show to the best advantage the difference in temperature between the east and west limbs of the planet.

During the first part of August usually no measurements were made until the large dark region, *Syrtis Major*, had passed from view. However, on August 6th, the *Syrtis* was on the centre of the disc, and although the east and west limbs appeared equally illuminated, the latter was the hotter.

The observations of August 15th are especially interesting because a bright region was on the west limb, and a dark region was on the east limb. Nevertheless the west limb was the hotter of the two.

(*c*) *North and South Polar Regions.*—The measurements of this year have verified the observations of 1922, showing that the north polar region is cooler than the south polar region, in summer.

Using the 53.3-ft. focus and the smallest receivers, it was possible to practically isolate the polar caps. The water-cell transmissions increased then to practically that of the direct solar radiation, showing that no planetary radiation, relative to the sky, is emitted from the polar caps. This is especially true of the north polar cap, which shows a systematically lower water-cell transmission than the south polar cap. The latter was probably covered with clouds which prevented the escape of planetary radiation.

The unusually high values of the water-cell transmissions of August 17th and 21st might be owing to an excessive out-going radiation from the thermocouple to the planet relative to the sky. In reality they are probably owing to mixed light from adjoining regions, also to poor seeing and the consequent difficulty in setting accurately on the extreme edge of the planet. This, with the difficulty in focussing, might introduce systematic errors in setting the receiver on the disc. The same might be true of the south polar region, the low value of the water-cell transmission being due to the fact that the image of the white polar cap was smaller than the thermocouple receiver. No doubt if the south polar cap could have been measured earlier in the season before it had melted and receded to such small dimensions, the water-cell transmissions would have been more accurate in indicating prevailing temperature conditions over it.

The polar caps are too steady in position and in outline to be composed entirely of clouds. It is generally assumed, from the way they shrink in size, that the polar caps are composed of snow and hoar frost. The water-cell transmissions show that the caps emit no planetary radiation, which is to be expected if they are composed of snow.

The only tenable explanation of the polar caps is that the more persistent parts are composed of snow and ice deposited on the surface of the planet. It is well known that the polar caps melt in the Martian summer and form again in the Martian winter. The making cap is of indefinite contour. It is a misty white, merging gradually into the surrounding land. The melting cap, on the other hand, is of definite contour and is bordered by a blue belt which retreats with the cap. A very extensive and minute study of the polar caps at the present and past oppositions, based upon visual and photographic observations at the Lowell Observatory, shows beyond any doubt that the true polar caps are not attributable to such atmospheric phenomena as mists and clouds. However, it is true that at certain seasons, and also occasionally at other times, the polar regions and caps are concealed from view by mists and clouds. Generally speaking, mists and clouds are more prevalent during the deposition of the cap, and as a rule the cloud-covered cap is not as brilliant as the true cap deposited on the surface. The well-defined contour of the polar snows becomes evident after the mists and clouds clear

away. When either cap begins to shrink, there proceeds to surround it a dark border or belt. It is thus seen that the atmospheric phenomena associated with the polar caps are readily recognized. In fact, the existence of the true polar caps deposited on the surface, and the occurrence at certain times of the superposed caps of clouds and mist (and occasionally the presence of hoar frost) mutually furnish conclusive evidence of the existence and the part played in the observed appearance of the polar regions by these different agencies and conditions. During the Martian summer there are no accretions to the caps, and only rarely do we have veilings and obscurations by clouds, partially obstructing clear views of the surface and contour. To the investigator who has access to complete observational data the conclusion that the caps are wholly atmospheric phenomena appears to be as ill-founded as the now exploded and untenable hypothesis that the caps are deposits of carbon dioxide snow. Let us, for example, consider the south cap, exposed to view during the present measures. As it melts and recedes during the Martian summer, lanes and bays form near the edge, in different longitudes, and with the advance of summer and further progress of the melting, isolated portions are left behind, to disappear later. Invariably, as the cap becomes smaller in size, its eccentric position becomes more marked with respect to the geographic pole—a characteristic not shared by the northern cap which sits squarely on its pole. At oppositions of similar presentation of the planet's surface, and at the same season of the planet's year, the same appearances recur with remarkable fidelity. It has been definitely established by visual and photographic observations that the details of the melting away and the disintegration of the cap take place in the same way, time after time. The lanes, bays, and detached remnants are found in the same latitudes and longitudes at the same Martian dates; thus showing, by repeating the same characteristics of outline and the same fixed markings within, at each Martian season, that the phenomenon does not have any of the variabilities common to clouds and atmospheric disturbances but, on the contrary, the regularity of behavior of a solid deposit of ice or snow, on the planet's surface.

Photographs taken with violet light are a ready means for detecting the attenuated atmosphere, clouds, and ice spicules which may be suspended in the air; but from the very nature of

the reaction on the photographic plate, the polar caps will have an enlarged hazy outline, merging into that of the overlying atmosphere. This is owing to the great brilliancy of, and the distribution of intensities of the light diffusely reflected from, the polar caps; also to the irradiation and the speed of reaction, with intensity of light, on the photographic plate. Hence, the interpretation of a photographic impression taken with blue light is difficult and likely to confuse matters. On the other hand, photographs taken in red light show the solid deposits forming the true polar caps, mentioned in the foregoing discussion, and confirms the visual observations.

A good example of a decrease in the water-cell transmissions with decrease in size of the south polar cap is the series of measurements of August 28th and of September 13th, as compared with the observations made a fortnight earlier. In spite of large experimental errors of observation, the measurements seem to show a gradual warning of the south polar region, as summer approaches, whereas the north polar region remains at a low temperature—the water-cell transmissions being the same as (or even higher than) that of the direct solar radiation.

The measurement of the radiation from Mars was concluded by repeating the measurements at the 18-ft. focus. The data, given in Tables V and VI, show that with the approaching culmination of the Martian summer season (on October 5th) the water-cell transmission decreased from 39 per cent. in July to 27 per cent. in September (the low value of 25 per cent. on September 13th is the mean of three closely agreeing measurements and hence seems trustworthy), showing a considerable rise in temperature, amounting to 20° C., or even higher, as will be shown presently.

The foregoing measurements on isolated regions of Mars were made through the water-cell, whereas the temperature determinations relative to the Moon are in terms of the ratios ($A:B$, Table VI) of the planetary radiation components of the central part of the disc. If the selective emission is different for different parts of the planet, then it will appear more prominently in the ratio $A:B$ than in the transmissions through the water-cell. However, it seems the logical method of obtaining a direct calibration of temperatures of Mars against the Moon in

which the brightness and temperature varies with age and surface conditions.

The method of relating the temperature of the centre of the disc of Mars with that of the Moon by means of the spectral components of planetary radiation will be more fully explained in the next caption. In the meantime, it is of interest to convert into temperatures the water-cell transmissions of different parts of the surface of Mars. This is accomplished by noting the per cent. transmission through the water-cell (Table VI) and the temperature, from Fig. 3, corresponding to the ratio, $A:B$, of the components of planetary radiation observed on a given date. These water-cell transmissions and corresponding temperatures are plotted in Fig. 2, without distinction as to dark or light regions, although the dark areas usually give the highest temperatures.

The highest value of water-cell transmission (75.5 per cent.) is obtained when there is practically no exchange of planetary and sky radiation. This condition would, no doubt, occur at the north pole where the temperature would be as low as, if not lower than, −70° C., which is assumed to be the temperature of the terrestrial stratosphere, and is the value calculated by the fourth-power law of total radiation. The dotted curve, Fig. 2, would result from taking the temperature of the atmosphere −100° C.

Assuming that, when the water-cell transmission is 75.5 per cent., the temperature of the north pole is close to −70° C., a curve is drawn as shown in Fig. 2. In this manner the water-cell transmissions which are higher than 35 per cent. of Table V can be translated into temperatures. These temperatures are indicated in the circular diagram in Fig. 2, in which the black dots indicate the positions of the thermocouple receivers. In view of the fact that the ice was melting and the polar cap was receding, it is evident that the temperature of the south polar region was up to 0° C. instead of the value −60° C. as observed through the overhanging canopy of water vapor or ice spicules which are in the polar atmosphere. After Martian solstice, October 5th, the temperature of the south polar region was up to +12° C.

It is to be understood, of course, that these receivers intercepted a considerable portion of the disc, as indicated in the "remarks" in Table V. The irregular decrease in temperatures from the centre to the western limb (18°, −5°, and 10° C.,

respectively), observed on September 12th, is probably attributable to errors of observation. However, it might be owing to clouds, the presence of which is frequently observed on Mars.[55]

In connection with the foregoing discussion, it is relevant to emphasize that the transmissions, and the temperature estimates, will depend upon the area of the receiver relative to the size of the disc-image, as may readily be seen by inspection of the temperature data, illustrated in Fig. 2. At best the smallest receiver intercepted about 490 miles of the circumference, or about 187,000 square miles. Slight changes in cloudiness on Mars will affect the measurements. With the rapid drop in temperatures as we approach the poles, it seems evident that these temperature estimates, uncorrected as they are for change in latitude, are too low.

To recapitulate, the foregoing measurements show that the morning side of the planet is at a lower temperature than the afternoon side, which has been exposed for a longer time to the Sun's rays. The dark regions show a temperature which is perhaps 15° to 20° C. higher than the light ones. With the advance in the summer season the southern hemisphere shows a gradual rise in temperature.

Further measurements should be made on selected areas, especially on the dark phases of the planet. The water-cell measurements on the morning side of the planet, when there was no phase (August 23rd), show that, as viewed through the Martian atmosphere, the temperature was −45° C. It would be especially instructive to have measurements on the entirely dark phase of Mars when it is on the east limb, to determine its temperature conditions, just as it is approaching sunrise. For example, on September 12th, when the dark phase was barely perceptible on the east limb (illuminated surface 0.976) the water-cell transmission was 66.3 per cent. (temperature, −60° C.) as compared with 55.8 per cent. on August 23rd, when there was no phase. From this it appears that the temperature of the unilluminated surface will be found quite low. That the temperature on the west limb is much higher than on the east limb is shown in the measurements of August 1st, when there was a small dark phase on the west limb, while the east limb was irradiated for an hour or more

[55] SLIPHER: *Pop. Astron.*, **29**, Feb., 1921; *Publ. Astronom. Soc. Pacific*, **34**, p. 215, 1922.

before this part of the planet turned into view. On this date the temperatures were −2° C. and −20° C., respectively.

From the foregoing, it is apparent that each renewed investigation begets new problems requiring solution, some of which must wait months and perhaps years before the planet is in the proper phase for measurement.

An interesting observation is the very large diurnal variation in temperature of more than 75° C., which is attributable to the rare atmosphere on Mars. At aphelion, when the intensity of the solar radiation on Mars is only about 0.69 that of the present position, the above-mentioned temperatures would be lower.

2. METHODS OF DETERMINING TEMPERATURES ON THE IRRADIATED SURFACE OF MARS.

In the foregoing section of this paper it was shown that under the same conditions of irradiation, under a noonday sun, the planetary radiation emanating from, and presumably the temperature of the conspicuous dark regions on, Mars was higher than that of similarly situated bright regions.

Under the present caption data and arguments are assembled which establish temperature levels of the brightly irradiated surface. Not until we obtain radiation measurements on the entirely dark phase on the eastern limb of Mars, as already mentioned, can an estimate be made of the temperature of the dark opposite side of the planet. However, the temperatures observed on the partially darkened eastern limb indicate great cooling on the dark side of the planet.

(*a*) *Temperatures Inferred from Radiation Exchanges.*—In a foregoing caption (which will be published in the complete paper) on a criterion for distinguishing planetary from sky and nocturnal radiation, data are presented showing that the low-temperature radiation from the planet is greatly in excess of that of the sky; also that it is comparable with that of the Moon. In our preliminary announcements of this year's results these measurements were interpreted as a qualitative test indicating that the excess incoming planetary radiation was from a source at a temperature of about 15° C. While this may be true by coincidence, it would probably not be true as a general principle. Hence, since the test was qualitative and since we have three other well-established methods for arriving at the planetary temperatures,

this qualitative test is not stressed in this more complete survey of work.

(*b*) *Temperatures Derived from Comparisons with the Moon.*—The temperature of the Moon is generally conceded to be much higher than that of the Earth. It is therefore a good planetary object to use as a temperature fixed-point for calibrating the radiometer.

In a previous communication [56] the question was raised as to the amount of selectivity reflected solar radiation there is mixed with the Moon's proper radiation of wave-lengths 8 to 15μ. Assuming an emissivity of 0.1, which was known to be less than that of minerals, it was found that even in this extreme case the emitted lunar radiation would be sixteen times the intensity of the selectively reflected solar radiation. If a higher emissivity coefficient had been used, say 0.8, then the emitted radiation would have been 128 times the reflected solar radiation. In the preceding paper on planetary radiation [57] the subject was again considered and it was then concluded that, while the existence of such a selective reflection must be admitted, the effects can be neglected in these investigations.

In a recent paper on the temperature of the Moon, Dietzius [58] failed to notice that in the above-mentioned calculation the value of the coefficient was intentionally taken too low. Indeed, he seems to have misinterpreted the whole paper. For he concluded (*loc. cit.*, p. 195) that Coblentz held to the belief that the Moon's temperature was as low as −200° C. when, as a matter of fact, in the above-cited papers the latter had calculated an effective average temperature of +82° C. for the full Moon, and had not even mentioned a temperature of −200° C.

Dietzius' contribution to the subject is a new calculation of lunar temperatures, using the most recent value of the solar constant of 1.94 g. cal. instead of 2.1 g. cal. per cm.^{2} used by Coblentz. From these calculations he derives temperatures ranging from −79° C. immediately preceding lunar sunrise, to 111° C. at lunar midday. His value of −79° C. is in good agreement with our measurements of the unilluminated part of the Moon, which

[56] COBLENTZ: *Phys. Rev.*, **24**, p. 307 (see p. 315), 1907; *Publs. Nos. 65 and 97*, Carnegie Inst. of Washington.

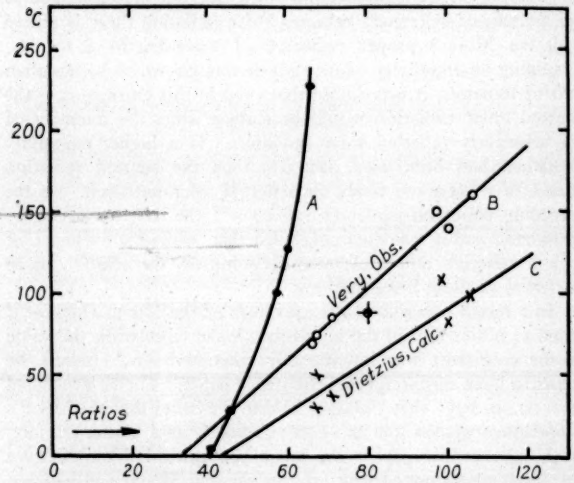
[57] *B. S. Sci. Papers* (No. 460), 18, p. 549, 1922.

[58] DIETZIUS: *Sitzber Akad. Wiss.*, Wien, **132**, p. 193, 1924.

produced no galvanometer deflection showing that the temperature is below that of the Earth's stratosphere, which is about −70° C. As already mentioned, Menzel's [59] calculations, based upon our water-cell transmissions, show that the Moon is very hot, possibly 120° C.

The first experimental determination of the Moon's temperature was made by Langley,[60] who compared the spectral energy

FIG. 3.



Calibration curves showing temperatures and corresponding ratios of spectral components of planetary radiation: *A*, calculated black body; *B*, observed on Moon; *C*, calculated by Dietzius.

distribution of the radiation from the Moon with the radiation from a Leslie cube at a temperature ranging from −2° C. to +178° C. The most reliable spectrum comparisons with this blackened screen showed an average lunar temperature of +45° C. near the time of the full Moon.

For the present investigation Very's [61] measurements (also Dietzius' calculations) on the Moon are especially useful. From

[59] MENZEL: *Astrophys. Jour.*, **58**, p. 65, 1923.
[60] LANGLEY: *Mem. Nat. Acad. Sci.*, **4**, p. 197, 1887.
[61] VERY: *Astrophys. Jr.*, **8**, pp. 199 and 265, 1898.

his data curves were drawn of the effective lunar temperature at an angle i from the subsolar point, and at various ages of the Moon. One particularly useful curve pertained to the angle $i = 40°$ where the estimated lunar temperature at first quarter was 74° C., and 98.4° C. at the third quarter. At an age of eleven days the lunar temperature was 124° C., and at sixteen days it was 170° C. Using curves of this type, as illustrated in the upper part of Fig. 4, an estimate was obtained of the temperature at different ages of the Moon. These temperatures and the corresponding ratios of the spectral components are given in Table IV, and plotted to scale in Fig. 3, curve *B*. In Fig. 2 the water-cell transmissions are plotted against temperatures, the value of −70° C. for a water-cell transmission of 75.5 per cent. representing conditions when there is no exchange of planetary and sky radiation. The lower part of this calibration curve is relatively unimportant in this work, but is invoked merely as a check on our temperature estimates.

(To be Continued.)

THE PART played by men of science in the political life of France is no inconsiderable one. It was the great mathematician, Painlevé, who was defeated last June for the presidency of France by Doumergue, and who was thereupon elected to preside over the Chamber of Deputies. He has quelled many stormy sessions by putting his hat on his head, thus adjourning the Chamber. After the retirement of Herriot he has recently succeeded in forming a cabinet and is now prime minister of the Republic. The story runs that, since the death of Poincairé, the physicist and mathematician, he found no one remaining to be worthy of his steel, so that he has entered politics as a diversion.

Emile Borel, member of the Institute and professor at the Sorbonne, is a deputy from the department of Aveyron. At his instance the Chamber last February voted the "sou of the laboratories," a tax of 5 centimes on every sum of 100 francs paid as salary in commerce and industry. From this an income for the laboratories of 12,000,000 francs is expected. The Right joined the Left in the passage of this bill designed to rehabilitate the scientific researches of France, which had of necessity suffered as a consequence of the German invasion. About two years ago contributions were made for the same purpose in connection with the celebration of the birth of Pasteur.

G. F. S.

The Thermal and Electrical Conductivities of Some Pure Metals. F. H. SCHOFIELD. (*Proc. Roy. Soc.*, A 742.)—As far back as 1853 Wiedemann and Franz proposed the relation that for all metals the ratio of the thermal to the electrical conductivity is the same. This was supplemented about a score of years later by the contention of Lorenz, based both on theory and experiment, that this ratio is proportional to the absolute temperature. This more comprehensive relation was confirmed by findings drawn from the electron theory by Drude, J. J. Thomson and H. A. Lorentz and by many experimental results. If the thermal conductivity be divided by the electrical and this quotient be, in turn, divided by the absolute temperature at which the two conductivities were measured, we get a function that "is sensibly the same for the pure metals, with perhaps a slight tendency to fall with decreasing temperature," so long as the range of temperature is from −100° to +100° C. "Below −100° C., the function shows an increasingly rapid fall with temperature and a considerable divergence between individual metals. Above a temperature of +100° C. very few determinations of thermal conductivity have been made, and the object of the present series of experiments has been to measure, in this region, the thermal and electrical conductivities of a number of metals of the highest purity obtainable commercially."

A rod of the metal under investigation was heated by an electric current in a coil embedded at its centre. A tube of metal surrounded the rod and it, too, was supplied electrically with heat at its middle, but the coil in this case was wrapped on the outside. The coils were placed as they were in order that each should directly affect only the metal it was intended to heat. Adjustments were made so that each part of the rod was surrounded by a portion of the tube at the same temperature as itself. Thus any lateral loss of heat from the rod was obviated. Thermocouples along the rod gave the temperatures at different points. From the flux of heat and the gradient the thermal conductivity can be computed. The electrical conductivity of the specimen rods was measured to a satisfactory accuracy by a fall of potential method.

Aluminum and copper were measured up to 600° C., nickel to 700°, magnesium to 400° and zinc to 300°. "The thermal conductivity of aluminum was found to increase with rising temperature, that of nickel to decrease at first and then above 500° C. to show an increase. The other metals, namely, copper, magnesium, zinc, showed on the whole slight decreases of conductivity with temperature. The values of Lorenz's function for copper, magnesium and zinc were practically constant at all temperatures; that for aluminum showed a rise with increasing temperature; that for nickel showed a rise to 300° C., above which temperature it remained nearly constant, except for an abnormal value at 400° C." G. F. S.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

THE DEVELOPING EQUIVALENCE OF SODIUM AND POTASSIUM CARBONATES.[1]

By S. E. Sheppard and P. A. Anderson.

SENSITOMETRIC development tests upon cine negative and portrait emulsions indicate that the substitution of a molecularly equivalent quantity of potassium carbonate for the sodium carbonate of a standard elon-hydroquinone developer does not appreciably alter the developing power of that developer.

The Auroral Green Line. (*Nature*, March 14, 1925.)—PROFESSOR MCLENNAN cabled a statement that he, working with Mr. Schrum in the cryogenic laboratory of the University of Toronto, has actually obtained and photographed the famous auroral green line. Its wave-length is 5577.35 A.U., and it was emitted by mixtures of air and helium and of oxygen and helium. It could not be obtained from oxygen, nitrogen, hydrogen or helium separately. The pressure in the tube, in which the electrical discharge passed through the gas, was about 5 mm. of mercury. This tube was jacketed with liquid air. The line was sharply defined.

For more than a year the auroral line has attracted much attention. Professor Vegard, the Norwegian physicist, from theory was led to predict the existence of solid nitrogen in the upper portions of the atmosphere. In the laboratory he bombarded solid nitrogen and believed that he got the green line of the aurora whose origin had been a mystery. One of the most interesting announcements made at the meeting of the British Association a few months later was to the effect that McLennan and Schrum had repeated the experiment and had failed to get the auroral line from nitrogen, though they had obtained lines not far from it. Vegard replied by claiming that the negative conclusion reached was not unimpeachable, alleging reasons for his statement, and the discussion has been continued in the scientific periodicals.

It is to be noted that the line as recently produced in Toronto was not obtained from a mixture containing nitrogen. Moreover, since the temperature of liquid air is not sufficiently low to solidify oxygen and much less to solidify helium, the line was not emitted by a solid. G. F. S.

* Communicated by the Director.

[1] Communication No. 232 from the Research Laboratories of the Eastman Kodak Company and published in the *B. J. Phot.*, **72**: 232, 1925.

The Coefficient of Viscosity of Water in Absolute Units. LEROUX. (*Comptes Rendus*, March 23, 1925.)—By the method of a rotating cylinder and with the utmost precautions a series of determinations of the coefficient of viscosity was made from 0° to 50° C. For this range the value drops from .0178 to about one-third as much, .0057. There is no trace of an anomaly near the temperature of maximum density. Furthermore no effect of velocity upon viscosity amounting to as much as ½ per cent. was detected.

G. F. S.

The Natural and the Artificial Permanent Magnetization of Rocks. F. LOEWINSON-LESSING and V. MITKEWITCH. (*Comptes Rendus*, March 23, 1925.)—About the beginning of the present century Folgheraiter in Italy made a study of the magnetization of pottery and of rocks and deduced some interesting conclusions as to the secular changes in the direction of the earth's magnetic field. The problem is now taken up afresh by other investigators. In the volcanic group of Karadagh in the Crimea, north and south poles in the rocks are found mingled within a small compass. This seems to indicate that this magnetization cannot be due to the magnetism of the earth but to some influence that can vary from place to place. It is known that a discharge of lightning may produce magnetization where it falls. The authors raise the question of its producing permanent magnetism at some distance from the path of the discharge. Calculation showed that the magnetizing force is adequate to cause at some dozens or hundreds of metres from the stroke a magnetization in rocks as strong as that observed in nature. The authors proceeded to subject their deduction to the test of experiment, using an electromagnet to provide the magnetizing force. Among other things they found that granites can be artificially magnetized, 61 per cent. of metamorphic rocks show no natural magnetization but can acquire an intense artificial magnetism and that sedimentary rocks in general have no natural magnetization and, indeed, cannot be magnetized. As the outcome of their inquiries the investigators are confirmed in attributing to lightning discharges the magnetization they discovered in the Crimea.

They put to themselves the further question, "Is there any way to distinguish the magnetization due to the earth's field from that caused by lightning?" They argue that a rock magnetized by a lightning discharge near to it ought to be so well saturated that their electromagnet can add but little to its magnetic strength, while those rocks that owe their magnetism to the relatively feeble field of the earth are capable of being much more strongly magnetized by the action of the electromagnet. They find, as was to be expected, examples of both kinds of rocks. The specimens from Karadagh could not be more strongly magnetized.

The doubt may well arise whether the lapse of time might not play an important rôle and whether all possible sources of magnetization have been considered.

G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

RADIO-DETECTOR MINERALS.[1]

By Edgar T. Wherry.

[ABSTRACT.]

ABOUT seventy-five minerals which have been found to possess radio-detector properties are tabulated with respect to their compositions. Sulphides are usually better than oxides of the same metals; selenides are sometimes better than sulphides. Most of these minerals are moderate conductors of low-voltage electricity. The theory of Roberts and Adams that sensitive spots on crystals are merely layers composed wholly of one kind of atom, is shown to be insufficient, and a modification is suggested. In some cases such layers are perpendicular to "hemimorphic" or polar axes, and the detector properties may be due to the corresponding one-sided attraction of the electron layers. In most minerals the presence of certain impurities improves the detector properties, which may be due to resulting irregularities in the crystal structure, with corresponding one-sided attractive forces holding groups of electrons.

PAINTING ON THE FARM.[2]

By H. P. Holman.

[ABSTRACT.]

THIS bulletin calls attention to the importance of regular painting for preservative purposes. It tells when to paint, how to paint, how to prepare surfaces for painting, and how to estimate the quantity of paint needed. It discusses the composition of paints, to the end that buyers may read intelligently the labels of ready-mixed paints and paint materials. It describes the principal kinds of ready-mixed paints, stating which kinds are best adapted for various purposes, and tells how to mix paints of various kinds and colors from available materials. Varnish, calcimine and cold-water paints, and whitewash are here included under the general term "paint."

* Communicated by the Chief of the Bureau.

[1] Published in *Am. Mineral.*, 10 (Feb., 1925) : 28.

[2] Issued as *U. S. Dept. Agr. Farmers' Bull. 1452*, April, 1925.

THE QUANTITATIVE DETERMINATION OF MOISTURE IN WHEAT FLOUR.[3]

By G. C. Spencer.

[ABSTRACT.]

EXTENSIVE tests indicate that the determination of moisture in flour by drying in hydrogen, in an air oven, or in a vacuum oven by the usual procedures is not satisfactory. The advantage of using loosely covered dishes in vacuum drying is shown. A thoroughly tested method, involving the use of a definite partial vacuum, is suggested as a standard. The rapid method proposed for the determination of moisture in flour gives results that agree closely with those obtained by the proposed vacuum method, and the time of operation is reduced from five hours to one hour. The necessary apparatus is easily installed, and the cost of upkeep is low.

THE NON-VOLATILE ACIDS OF THE STRAWBERRY, THE PINEAPPLE, THE RASPBERRY AND THE CONCORD GRAPE.[4]

By E. K. Nelson.

[ABSTRACT.]

BY THE ester-distillation method it was found that the acids of the strawberry were citric acid (about 90 per cent.) and l-malic acid (about 10 per cent.); and that the pineapple acids were citric acid (about 87 per cent.) and l-malic acid (about 13 per cent.); that in the red raspberry the acids were a mixture of citric acid (about 97 per cent.) with l-malic acid (about 3 per cent.); and in the black raspberry the acid was citric acid. The acids of the Concord grape were a mixture of l-malic acid (about 60 per cent.) and d-tartaric acid (about 40 per cent.).

Pharmacology of Alcohol.—Recent work by REID HUNT, of Harvard University (*Ind. Eng. Chem.*, 1925, xvii, 427), indicates that the toxicity of illicit liquor is due to its alcohol content rather than to the very small amount of acetaldehyde which is present. A rather small margin exists between the amount of alcohol required to produce deep intoxication and that sufficient to produce death. Methyl alcohol or methanol is far more poisonous than ethyl alcohol; poisoning by methyl alcohol is due to the action of that compound itself, and not to the presence of impurities in it. J. S. H.

[3] Published in *J. Assoc. Official Agr. Chemists*, **8** (Feb., 1925): 301.

[4] Published in *J. Am. Chem. Soc.*, **47** (April, 1925): 1177.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, May 20, 1925.)

HALL OF THE FRANKLIN INSTITUTE,

PHILADELPHIA, May 20, 1925.

DR. WILLIAM C. L. EGLIN, President, *in the Chair.*

Additions to membership since last report, 20.

The Chairman announced that the business of the meeting would be the annual presentation of the Franklin Medal in recognition of distinguished scientific and technical achievements. He recognized Dr. Karl T. Compton, of Princeton University, who made a statement of the work of Dr. Pieter Zeeman, of the University of Amsterdam, recently awarded the Franklin Medal, "in recognition of his numerous and important contributions in the field of magneto-optics and particularly of his discovery of the effect of a magnetic field upon the frequencies of the light from a radiating source."

Mr. A. Loudon, Secretary, Royal Netherland Legation, Washington, D. C., representing the Netherland Minister Jonkheer Dr. de Graeff, was then presented to the Chairman and received from him the Franklin Medal, accompanying certificate and Certificate of Honorary Membership in the Institute, awarded to Dr. Pieter Zeeman. Mr. Loudon expressed appreciation of the high honor conferred upon his distinguished countryman.

Dr. E. W. Rice, Jr., General Electric Company, was then recognized and described the work of Dr. Elihu Thomson, of Lynn, Mass., who had been awarded the Franklin Medal "in recognition of his pioneer work in the field of electricity and electrical engineering and of his numerous inventions in these fields."

Doctor Thomson was then presented to the Chairman and received from him the Franklin Medal, accompanying certificate and Certificate of Honorary Membership in the Institute. Doctor Thomson expressed his thanks for the honor conferred upon him.

Dr. Arthur W. Goodspeed, of the Institute's Board of Managers, was then recognized, and introduced to the Chairman the Honorable William Cameron Sproul, ex-Governor of Pennsylvania, who had been elected to Honorary Membership in the Institute. The Chairman presented the Certificate of Honorary Membership to Doctor Sproul, who expressed his appreciation of this recognition.

Doctor Compton then read the paper on the "Magnetization of Spectrum Lines," prepared by Doctor Zeeman for the occasion.

Doctor Thomson then presented his paper on "The Mechanical, Thermal and Optical Properties of Fused Silica."

Adjourned.

HOWARD MCCLENAHAN,
Secretary.

(A full account of the meeting will appear in a later issue of the JOURNAL.)

HOWARD McCLENAHAN, E.E., M.S., LL.D.,

APPOINTED SECRETARY.

At the Stated Meeting of the Board of Managers held on Wednesday, May 13th, Dr. Howard McClenahan was appointed Secretary of the Institute.

Doctor McClenahan was born in Maryland in 1872, was a member of the Class of 1894 in Princeton, received the graduate degree of E.E. in 1895, and spent the year 1895–1896 in practical electrical engineering. He then returned to Princeton for additional graduate work, at the end of which he received the degree of Master of Science in June, 1897. He was appointed instructor in Physics in 1897, instructor in Electrical Engineering as well in 1899, assistant Professor in Physics in 1902, and Professor of Physics in 1906. He was appointed Dean of the College in 1912 and will relinquish that office, as well as his Professorship in Physics, at the close of the present college year.

He was a charter member of the American Physical Society, is a past President of the Association of Colleges and Secondary Schools of the Middle States and Maryland, and is a former Chairman of the College Entrance Examination Board, of which he was a member for twelve years, as Princeton's representative.

Doctor McClenahan has carried on the teaching of Physics and Electrical Engineering in Princeton for twenty-eight years. He is the author of "Laboratory Directions in Experimental Physics," was largely responsible for the design and construction of the Palmer Physical Laboratory in Princeton, and was solely responsible for its extensive equipment. He was the original designer of the very unusual and unusually large systems of electrical wiring for experimental purposes. He has been the Secretary of the Department of Physics in Princeton for twenty-three years.

During his term as Dean of the College, Doctor McClenahan has been noted for the fairness of his dealings with the students. As a student himself he was a member of the first Honor Committee in examinations which Princeton had. As Dean he has had complete supervision of the maintenance of the honor system and has extended the spirit of that system to all undergraduate affairs. He is the author and developer of the whole system of student self-government in Princeton University, which system is singularly successful.

During the war period Doctor McClenahan went to Europe as the representative of Princeton University in order to study the conditions of Belgian relief and other relief work. After his return he was very active in aiding the work of the Belgian Relief Commission and as the head of the Red Cross movement in and about Princeton. He was made Officier de l'Ordre de la Couronne by King Albert of Belgium in recognition of his helpful services.

Doctor McClenahan is a member of the Board of Trustees of Lincoln University and a member of the Board of Counsellors of the Gunnery School.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, May 6, 1925.)

HALL OF THE INSTITUTE,

PHILADELPHIA, May 6, 1925.

MR. HAROLD CALVERT *in the Chair.*

The following report was presented for final action:

No. 2835: Plastometer.

The instrument considered in this investigation is designed to give a measurement of the relative hardness of bodies composed of such materials as india rubber and others that are deformed temporarily under a medium pressure.

The specific purpose of the device is the measurement of the hardness of the rubber-covered rolls used in paper-making machines. It is well known that elasticity, plasticity, density, etc., are qualities that affect the hardness of rubber and that the surface of a rubber-covered roll is affected by time and use particularly by a loss of elasticity.

The sub-committee of investigation made tests with the instrument and obtained reports from users concerning its value in the industries and in consideration of the ingenuity displayed in its design, and its adaptability to the measurement for which it is used, recommended the award of the Certificate of Merit to Benjamin D. Coppage, of Wilmington, Delaware.

The report and recommendation were adopted.

The following reports were presented for first reading:

No. 2829: Midgley Optical Indicator.

No. 2836: Work of C. T. R. Wilson in Making and Recording the Tracks of Ionizing Rays.

GEORGE A. HOADLEY,
Acting Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, May 13, 1925.)

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MR. CHARLES H. WHITNEY, 3235 North 17th Street, Philadelphia, Penna.

NECROLOGY.

Dr. David T. Day, 715 Nineteenth Street, N. W., Washington, D. C.

Charles Gordon Buchanan, mechanical engineer and President of the C. G. Buchanan Company, Inc., 90 West Street, New York City, died recently at his son's home in East Orange, N. J., in his sixty-ninth year. He was born in New York City, September 25, 1856, and was educated in the public schools of that city and at Stevens Institute. For many years he was engaged in general engineering work. From 1884 to 1887 he was interested in mining and mill

building in Montana and Idaho, and from 1887 to 1889 he was associated with The Beckett Foundry and Machine Company, of Arlington, N. J. About 1900 his activities were centred about New York and Philadelphia, when he became associated with, and was Consulting Engineer for, the George V. Cresson Company, whose plant was located in the latter city. As Mr. Buchanan had brought out a number of patents on crushing and magnetic separating machinery, and had developed a large demand for this type of equipment, the C. G. Buchanan Company was formed in 1902, and Mr. Buchanan was President of this organization until his death.

While essentially an engineer, Mr. Buchanan was also a musician and connoisseur of old violins, and was interested in literature and art. He was a member of the American Iron and Steel Institute, the American Institute of Mining and Metallurgical Engineers, and Vice-chairman of the Board of Directors of the Manufacturers' Division of the National Crushed Stone Association.

Mr. Buchanan became a member of The Franklin Institute on January 25, 1902.

LIBRARY NOTES.

PURCHASES.

American Railway Association.—Locomotive Cyclopedia of American Practice. Seventh edition. 1925.

BABBITT, HAROLD E.—Sewerage and Sewage Treatment. Second edition. 1925.

BORN, MAX.—Einstein's Theory of Relativity. Translated by H. L. Brose. No date.

CLAASSEN, H.—Die Zuckerfabrikation. Fifth edition. 1922.

Electrician: A Weekly Journal of Telegraphy, Electricity, and Applied Chemistry. Volumes 1–4. 1862–1863.

FRITH, JULIUS, and BUCKINGHAM, FREDERICK.—Vibration in Engineering. 1924.

FRÜHLING, R.—Anleitung zur Untersuchung der Rohstoffe, Erzeugnisse, Nebenerzeugnisse und Hilfstoffe der Zuckerindustrie. Ninth edition by A. Rossing. 1919.

GILLETT, H. W., and MACK, E. L.—Molybdenum, Cerium and Related Alloy Steels. 1925.

GRÖGER, A.—Chemisch-technisches Vademekum für Zuckerfabriken. Volume 3, 1906–1910. 1911.

LADOO, R. B.—Non-metallic Minerals: Occurrence—Preparation—Utilization. 1925.

ROSBLOOM, JULIUS.—Diesel and Oil Engineering Hand-book. Third edition. 1925.

SCHALLEHN, C. A., Compiler.—Jahr- und Adressbuch der Zuckerfabriken Betriebzeit 1923/24/25 mit den Kunsthonigfabriken im deutschen Reiche. 53 und 54 Jahrgang. 1924.

WOHNRYZEK, OSKAR.—Betriebskontrolle der Zuckerfabrikation. Volume 1 1923.

BOOK REVIEWS.

FOUNDATIONS OF THE UNIVERSE. By M. Luckiesh, Director, Lighting Research Laboratory, General Electric Company. viii–245 pages, illustrated, 8vo. New York, D. Van Nostrand Company. Price, $8.

"Where wast thou when I laid the foundations of the earth?
Declare, if thou hast understanding,
Who determined the measure thereof, if thou knowest?
Or who stretched the line upon it?
Whereupon were the foundations thereof fastened?
Or who laid the corner-stone thereof
When the morning stars sang together?"

The title of this book suggests those of two other books of comparatively recent issue: Balfour's "Foundations of Belief" and Chamberlain's "Foundations of the Nineteenth Century." Both were efforts to set forth basic principles of human action, and both were somewhat lacking in impartial views. Luckiesh has no particular cause to defend, and is too well trained in scientific research to go astray from facts in general, but it cannot be overlooked that in writing upon such a wide subject there is a liability to accept data from others of which one has no personal knowledge of the trustworthiness. It is a question whether the book will be satisfactory to that now much-solicited person, "the average reader," who is supposed to be desirous of knowing all that modern science has ascertained. The essay is practically limited to physical and physico-chemical phenomena, the biologic phases being untouched.

The general method is to present the development of our knowledge from the historical point of view, in which necessarily only the more prominent steps can be considered. The evaluation of the work of a given investigator or of a given epoch in the world's progress requires close study and impartiality, and those not familiar with the methods of modern historians may go as far astray as a historian would in presenting the abstruse data of a well-developed science. In the preface, for instance, the story of Galileo is mentioned, but with incomplete presentation of it. Allusion is made in the book to the fable of Newton and the apple, though our author has evidently some doubts about the matter. The apple story has probably no more validity than the story of Washington and the cherry tree. No contemporary mention of it is known.

In presenting the many data with which the work is enriched the author seems to accept too readily the statements that have appeared in physics and chemistry of recent years. That a great many of the present views on the nature of the atom and the interrelations of the elements rest upon sound experimental foundation must be conceded, but enthusiastic workers have been led into speculations that cannot be regarded as worthy of serious consideration. We have, for instance, an allusion in this book to the "total mass of the universe." Surely, there are no data upon which such a figure can be reliably determined, and the statement is not worth the labor it takes to print it. Throughout the book there are allusions to the doctrine of relativity, but as with most of the efforts to make this doctrine plain to non-mathematical readers, the explanations do not fully explain. Luckiesh, indeed, says that beyond some simple ideas, mathematics alone can set forth the essence of Einsteinism.

There is an indication of haste in the preparation of the book, though the literary form is clear and correct. On page 103, a misleading paragraph is found. The impression is given that ionization is due to action of an electric current, but it occurs by the simple fact of solution or other physical change in which the molecules are freed from their mutual attractions, or perhaps, in view of the recent work on crystal structure, when molecules are arranged as expressed in the common formulas. It is also stated that water develops a positive hydrogen ion and a negative oxygen ion. The fact is that water ionizes to $\dot{H},\bar{HO}$, these existing in minute amount in the purest form. Lavoisier is given credit for the foundation of modern chemistry, presumably in echo of Wurtz's unfair sentence. No chemist will wish to detract from Lavoisier's service to the science, but the claim that he "founded chemistry" is grossly unjust to many other workers. It is impossible to determine in most cases to whom credit for origination of anything may be due. There are foreshadowings of discoveries and inventions throughout history, and modern historians do not favor the designation of epochs or regard particular individuals as bringing such epochs to pass. To speak of Lavoisier as the "founder of modern chemistry" is to pass by the work of Black, Scheele, Boyle, Priestley, and many others.

In one of the closing paragraphs the author makes a sort of confession of faith. Like many present-day scientists, confronted with the antagonisms of devout believers, who are trying to restrain the freedom of teaching for fear it may disturb the dogmatism of the creeds, Luckiesh rejects such dogmas, but falls back on the usual shibboleth of a vague deism that has no value in philosophy or morals.

HENRY LEFFMANN.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Fifth edition, Vol. III, revised, and in part rewritten. Edited by S. S. Sadtler, E. C. Lathrop and C. A. Mitchell, assisted by collaborators. ix–732 pages, numerous illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1925. Price, $7.50.

It is perhaps unwise to say that any particular volume of Allen's Commercial Organic Analysis is better than the rest, but at this time, the volume now issued is certainly most opportune. It covers the topics of hydrocarbons, bitumens, naphthalenes, anthracenes, phenols, phthaleins, phthalic acid and modern explosives, including, therefore, many substances that are attracting wide interest in war and peace. The intrusion of liquid fuel into the field heretofore monopolized by coal, has given rise to a vast amount of inventive effort and corresponding necessity for exact chemical methods. The development in this country of an active color industry has made all the data about the "coal-tar crudes" and the "intermediates" of prime importance and this book will be most welcome to all English-speaking chemists. Few persons, indeed, can realize the labor that is required to prepare such a work, but the editors are thoroughly familiar with the topics they have had in charge and their collaborators are equally equipped to deal with the special assignments. The progress of engineering chemistry since the appearance of the first edition is well shown by the extension of the section on asphalt, a substance, or rather a collection of substances, that is now entering largely into the "good roads" campaign so active in America.

The inclusion of a section on modern high explosives indicates the striking change that has come over that department of industry since the first edition of the work. While several of the nitro-compounds of explosive character were known at that time, especially guncotton and nitroglycerin, the intimate relation which now exists between the color and explosives industries had not developed. Indeed, it may be said that the real relation between them was not realized by the world at large until the late war. Germany knew, but the rest of the world learned by sad experience, how easy it is to turn a color factory into a munitions factory, and one of the points that the United States must note and bear in mind is that without careful encouragement of the types of industry covered in this volume we will be unprepared for the next war, which will probably be due to German desire for revenge and recovery of lost territory.

Analysts will welcome the appearance of the volume and will hope that the remaining ones will follow promptly, for the work holds the place which it attained on its first issue, *primus inter pares*. HENRY LEFFMANN.

THE MODERN SOAP AND DETERGENT INDUSTRY, INCLUDING GLYCEROL MANUFACTURE. By Geoffrey Martin, D.Sc. Vol. II, Manufacture of Special Soap and Detergent Compounds. London, Crosby Lockwood and Son, 1925. Price, 36s. net.

The general character of this book was set forth in the review of the first volume a few months ago. The construction of the work remains the same, the awkward system of paging separately each section being continued. What mischievous spirit entered into the mind of the maker of this book to lead to such an absurd system? As there is no index to the volume (presumably there will be a full index in the third) the searcher for data goes boggling through the book at about the point where he expects to find information. The several sections are indeed indicated at the bottom of the page in small type (it should have been at the top of the page in large type), but this is a confession that the system is insufficient. The work contains a great amount of information on the technology of detergents and their commercial forms. The paragraph on phosphate soaps is very brief and does not mention trisodium phosphate, which has some vogue as a detergent. HENRY LEFFMANN.

THE HEAVENS. By J. H. Fabre. Translated by Dr. E. E. Fournier d'Albe. 336 pages, illustrated, 8vo. Philadelphia, J. B. Lippincott Company, no date.

Fabre is well-known as a writer on natural history subjects. How far his statements in these fields are strictly correct may be a question of importance, but so far as the present book is concerned, he is obviously relying upon the works of competent astronomers, and it may be assumed, therefore, that the data are correct. The book presents the usual characteristics of popular works on astronomy now so familiar to the general reader. It is fairly comprehensive, including over 300 pages of closely but clearly printed text with many illustrations, both diagrammatic and in the form of plates. Considerable information is given concerning the principles of geometry as applied to the

survey of the earth and of the heavens and also many physical data of the celestial bodies. The work, therefore, taken as a whole, will be interesting and useful to those who desire to know about the recent dvelopments in astronomy.

HENRY LEFFMANN.

ELECTRICITÉ ATMOSPHERIQUE. Par B. Chauveau. Vol. 1. "Introduction Historique." 90 pages. Price, 10 francs. Vol. 2. "Le Champ Electrique de l'Atmosphere." 264 pages, illustrations. Price, 25 francs. Vol. 3. "La Conductibilité et l'Ionisation de l'Atmosphere." 240 pages, illustrations. Price, 22 francs. Three vols., illustrations, 8vo. Paris, Octave Doin, 1922, 1924, 1925.

The author's aim in writing this treatise has been to present a comprehensive account of the electrical phenomena of the atmosphere, a subject which he states has never received adequate representation in French scientific literature. He finds in fact that only two treatises on the subject, and of relatively recent date, exist in German, and none in English, except such articles by eminent specialists as have appeared in encyclopædias. The work represents the product of investigations in that field during a period of thirty years.

The author's first care has been to present the essential parts of the subject-matter by a work that appeals more particularly to meteorologists than to physicists, among the former of whom there are many earnest workers who have little familiarity with some of the later concepts of modern physics. That object has been kept in view in part 2, "Le Champ Electrique de l'Atmosphere," by avoiding considerations of ionization in dealing with fundamental phenomena. Again, the history of the development which is comparatively little known, has been treated at some length.

The work has accordingly been divided into three principal divisions:

First: A historic introduction in three chapters, giving the development of ideas and of methods during three characteristic periods. The first (1750 to 1860) from Franklin to Peltier; the second (1860 to 1899) from William Thomson to Exner and his pupils; in the third, figure prominently the names of Elster and Geitel and of Ebert.

Second: In this section are discussed an investigation of the electric field of the atmosphere and its regular and transient variations, the dissipation of the terrestrial charge into the atmosphere, and the measure of electric charges due to rainfall.

The essential fundamental facts, as well as the results of observation and measurements which relate to them, are treated independently of all theoretic interpretation.

Third: The third section deals with the investigation of the ionization and conductibility of the atmosphere, in the first two chapters of which the indispensable general data on ionization and radio-activity are set forth.

The work should appeal not alone to meteorologists whom the author has particularly in mind. Now that we travel *via* the air-route and receive audible messages by artificially produced electrical disturbances of the atmosphere, interest in the subject has ceased to be only academic except to the meteorologist. Particularly should the serious investigator in radio-transmission find profit in a perusal of these volumes.

LUCIEN E. PICOLET.

TECHNICAL MECHANICS, STATICS, KINEMATICS, KINETICS. By Edward R. Maurer, Professor of Mechanics in the University of Wisconsin, and Raymond J. Roark, Assistant Professor of Mechanics in the University of Wisconsin. Fifth Edition, rewritten, xii + 364 pages, 6″ × 9″, cloth, 559 illustrations. New York, John Wiley and Sons, Inc., 1925. Price, $3.50 net.

The modern college course in engineering imposes a severe stress upon the mental endurance of the student, and it is most desirable that the subjects prescribed be presented in such a manner as to effect the greatest economy of effort in their prosecution. The time-element is an important factor, the student must dwell upon the work he is doing at some length in order to acquire a real familiarity with it. It is in the reduction to a minimum of these inevitable periods of reflection that the value of a text-book is greatly amplified. This important matter which is secondary only to the technical value of the subject-matter, the authors have kept well in mind.

The work may be properly described as a formal text on the elements of mechanics with applications to engineering problems. The treatment is deductive and rigorous without oppressive formality, and well-illustrated detailed explanations illuminate the discussions of the various theorems and give them an interest which they would otherwise lack.

At the end of each section an illustrative example is given. These are worked out in detail with references to the text and are arranged in the good form suitable to serve as a model for the student to apply to his own work. Such examples are most helpful in insuring an accurate and ready appreciation of the full significance of a theorem. Drill-problems do not appear in the text, but a large number, well illustrated, are provided in an appendix at the end of the volume. Graphs and tabulated computations are freely used. The extensive employment of the latter emphasizes the value of this simple clerical device in keeping track of the various elements and successive steps of computations of considerable length.

In this comprehensive collection of mechanical theorems, the vibration of a mass acted upon by a force which varies as a function of its distance from a central point for some reason has been ignored, although its elementary treatment need not transcend the presupposed knowledge of trigonometry and simple calculus; vibration problems are of timely interest.

The character and execution of the work reflect credit alike upon the authors and publishers. LUCIEN E. PICOLET.

THE ELEMENTS OF MACHINE DESIGN. By S. J. Berard, Assistant Professor of Drawing and Machine Design, Brown University, and E. O. Waters, Assistant Professor of Machine Design, Sheffield Scientific School, Yale University. 323 pages, 6″ × 9″, cloth, 244 illustrations. New York, D. Van Nostrand Company. Price, $2.50 net.

For many years technical periodicals and the publications of engineering societies have recorded an uninterrupted flow of contributions to the art of machine construction and these sources, as well as compilations in book-form which have appeared from time to time, constitute an abundant store of information to which nothing need be added to meet the technical requirements

of current practice in the art. The work in hand is a text on the methods of proportioning machine parts which have been drawn from this copious source. It has been prepared for the use of students in engineering courses and others, properly qualified, who desire to become machine designers.

With that object, the authors have shown discrimination in their choice of subject-matter as representative of approved practice and wisdom in its arrangement. The first three chapters, covering forty-two pages, are devoted to the more commonly used data on structural elements, section moduli, typical beams, etc., and an excellent code of practice in the preparation and execution of a design, and of checking drawings. Each of the remaining twenty-five chapters with the exception of the last treats of some machine part of which the various types of representative practice are described and formulated. These are illustrated by excellent line-cuts reproduced from equally workmanlike drawings, and by half-tone cuts. The last chapter treats of drafting-room systems.

With each topic an illustrative numerical example is given, worked out in carefully arranged detail, which may well serve as a model to the student in arranging his notes as well as clarifying the explanations. A list of references is given at the end of each chapter. Among some of the notable features included in the text may be mentioned the account on limits, tolerance and allowance, the analysis of rivetted joints based on the A.S.M.E. Boiler Code and the adoption of the Lewis formula for the strength of gear teeth.

In the well-balanced section on gearing no mention appears to be made of the metric notation for diametral pitch. It is a relatively small matter, but since it is used by American manufacturers it might properly be mentioned. Again the inclusion of the open-belt method of design of cone-pulleys would be welcome to some users of a book of this kind. The omission of such topics as machine frames, thick cylinders, flat covers and springs will prove disappointing to a large number who will naturally expect to find them under such a broad title as "machine design." The typographical work throughout is of a high order of excellence. LUCIEN E. PICOLET.

RECENT PROGRESS IN ENGINEERING PRODUCTION. By C. M. Linley. 340 pages, illustrations, plates, 8vo. New York, D. Van Nostrand Company, 1925. Price, $10.

Manufacturing industries in recent years have adopted many of the methods for securing accuracy previously found only in the physical laboratory, and pieces of apparatus and not a few of the requirements in methods employed found in many modern shops were never dreamed of by the old-time mechanic. In contrast with former conservation, managers of up-to-date shops, particularly those devoted to large-scale production, are keenly appreciative of the possibilities offered by the contributions of the scientific laboratory. It is therefore essential that the manager who would have his shop at the highest point of efficiency or the engineer who would plan such a shop, should be *au courant* with those "vulgarized" laboratory appliances and methods which have become available for commercial use.

It is with these modern appliances and methods that the author deals in the forty-one chapters of his book. Each chapter is devoted to some particular

tool or process under such representative captions as "Grinding," "Metal Cutting by Machine-controlled Oxygen Jet," "Milling Machines," "Balancing of Parts of High-speed Machinery," "The Salving of Worn and Inaccurately Machined Parts." He has compiled a collection of modern methods, a detailed account of which could probably only be found scattered in many pages of technical periodicals.

The descriptions which are copiously and appropriately illustrated are not alone thoroughly informative, but they are also highly interesting from the many side-lights with which the accounts abound; the author is evidently very much at home with his subject. Being an English book, it naturally draws its examples from the products of firms of that country but by no means exclusively so, a considerable number of tools and instruments of American and some of continental origin being included, moreover lines of national demarcation of industrial products are rapidly disappearing; good engineering has no nationality.

The book is well printed in type of adequate size for comfortable use and the cuts, in general, are satisfactory, particularly the line-cuts. The half-tone cuts, however, are not of that superlative quality often found in modern trade catalogues, nevertheless they answer their purpose. The only objection that affects the individual purchaser is the rather high price and that may not be a valid one, for though there is no difficult type-work of algebraic formulas or tabular matter, the burden of collecting, verifying and editing the large array of valuable data presented has been undoubtedly a heavy one. The book should be in every library and on every engineer's shelf.

LUCIEN E. PICOLET.

SYNOPSIS OF APPLICABLE MATHEMATICS WITH TABLES. By L. Silberstein, Ph.D., xi + 250 pages, 5½" × 8½". New York, D. Van Nostrand Company, 1923. Price, $4.50.

The aim in producing this volume has been to meet the needs of the theoretical physicist and others who make extensive use of mathematical processes by a collection of mathematical formulæ, definitions and theorems, together with tables of the more important functions, such as elliptic integrals, Bessel functions and spherical harmonics, Fresnel functions and a few others.

Preceding the mathematical synopsis, sixty-eight pages are devoted to tables of the usual logarithms of numbers and trigonometric functions. The trigonometric tables are constructed on the decimal subdivision of the angular degree.

The inclusion of common logarithms and trigonometric tables is a usual addition to a book of this kind, as the author says "to make it a more complete *vade mecum* for the physico-mathematical worker." That is a good reason for including the tables, but as the author expresses regret that reasons of space made it impracticable to include a section on differential equations and other topics not considered, the space so occupied might better have been utilized for these omissions and for possible amplifications. Moreover such tables receive much more severe usage in the hands of an active worker than a reference-book and when printed separately replacement is a small matter.

The 182 pages of subject-matter contain an extensive collection of mathe-

matical devices in usable form, many of which are to be found only in special treatises. The abstract of the table of contents which follows is indicative of the character of this collection: Interpolation and Finite Differences; Roots of Some Transcendental Equations; Hyperbolic Functions and Table; The Sine-, Cosine-, and Exponential Integrals, Si x, Ci x, and Ei x; Fresnel's Integrals, with Table; The Error Function, with Table; The Gamma Function; Fourier Series and Fourier Integrals; Multiple Integrals; Functions of a Complex Variable; Spherical Harmonics; Bessel Functions and Tables; Elliptic Functions and Tables; Calculus of Probabilities, Theory of Errors; Differential Geometry; Non-Euclidean Geometry; Projective Geometry; Vector Algebra and Analysis; Quaternions, Tensor Calculus.

Despite the necessary condensation, explanations are given at some length, especially in the sections on geometry and on vectors. Frequent references to sources of information also appear in the text.

A work of this sort has another field of usefulness than that specified by the author. It constitutes an excellent syllabus for a course of study and for that purpose a bibliography which need not take much space would prove a valuable addition.

The difficult type-work entailed in the setting-up of the large number of algebraic forms has been accomplished with the characteristic excellence of the products of its noted publishers. L. E. P.

TIDES AND CURRENTS IN NEW YORK HARBOR. By H. A. Harmer, Assistant Chief, Division of Tides and Currents, U. S. Coast and Geodetic Survey. Special Publication No. 111. 174 pages, illustrations, maps, 8vo. Washington, Government Printing Office, 1925. Price, thirty cents.

The present volume contains the results of a comprehensive current survey made jointly by the Coast and Geodetic Survey and the United States Engineer Office, first district, New York, in the summer of 1922, and of previous tidal and current surveys made at various times. It includes much valuable data on tides and tidal phenomena in and about New York harbor, presented in such a way that it will be useful not only to the mariner, engineer and scientist, but also to the non-technical reader who has need for such information. Fifty-two illustrations, a number of them folded maps, add much to the value of the work.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 209, Characteristics of a Single Float Seaplane during Take-off. By J. W. Crowley and K. M. Ronan. 11 pages, illustrations, quarto. Washington, Government Printing Office, 1925. Price, five cents.

At the request of the Bureau of Aeronautics, Navy Department, the National Advisory Committee for Aeronautics at Langley Field is investigating the planing and get-away characteristics of an N-9H, a DT-2, and an F-5L, as representing, respectively, a single float, a double float, and a boat type of seaplane. This report covers the investigation conducted on the N-9H. The results show that a single float seaplane trims aft in taking off. Until a planing condition is reached the angle of attack is about 15° and is only

slightly affected by the controls. When planing it seeks a lower angle, but is controllable through a widening range, until at the take-off it is possible to obtain angles of 8° to 15° with corresponding speeds of 53 to 41 m.p.h. or about 40 per cent. of the speed range. The point of greatest resistance occurs at about the highest angle or a pontoon planing angle of 9½° and at a water speed of 24 m.p.h.

PUBLICATIONS RECEIVED.

Meteors, by Charles P. Olivier. 276 pages, illustrations, plates, 8vo. Baltimore, Williams and Wilkins Company, 1925. Price, $6.

The Heavens, by J. H. Fabre, translated by Dr. E. E. Fournier d'Albe. 336 pages, illustrations, plates, 8vo. Philadelphia, J. B. Lippincott Company, 1925.

Transmission Circuits for Telephone Communication: Methods of Analysis and Design, by K. S. Johnson. 326 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1925. Price, $5.

The Testing of High-speed Internal Combustion Engines, with special reference to automobile and aircraft types and to the testing of automobiles, by Arthur W. Judge. 392 pages, illustrations, plates, diagrams, 8vo. New York, D. Van Nostrand Company, 1925. Price, $7.50.

Foundations of the Universe, by M. Luckiesh. 245 pages, illustrations, plate, 8vo. New York, D. Van Nostrand Company, 1925. Price, $3.

The Volcanic Activity and Hot Springs of Lassen Peak, by Arthur L. Day and E. T. Allen. 190 pages, illustrations, plates, quarto. Washington, The Carnegie Institution of Washington, 1925.

Analytic Geometry and Calculus, by Bolling H. Crenshaw and Cincinnatus D. Killebrew. 222 pages, illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company, 1925. Price, $2.75.

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La Théorie de la Relativité restreinte d'Einstein et la Logique, par le Dr. J. H. Tummers. 20 pages, illustrations, 8vo. Venlo (Holland), 1925.

Measurements of Natural Light during the Solar Eclipse, January 24, 1925. Advance report presented at a meeting of the New York section of the Illuminating Engineering Society, April 9, 1925. 34 pages, illustrations, plates, 8vo. New York, Illuminating Engineering Society.

Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory near Tucson, Ariz., 1921 and 1922, by Daniel L. Hazard. 99 pages, diagrams, 8vo. Washington, Government Printing Office, 1925. Price, fifteen cents.

Results of Observations Made at the United States Coast and Geodetic Survey Magnetic Observatory of Vieques, P. R., in 1921 and 1922, by Daniel L. Hazard. 98 pages, diagrams, 8vo. Washington, Government Printing Office, 1925. Price, fifteen cents.

Specific Heat of Superheated Ammonia Vapor, by N. S. Osborne, H. F. Stimson, T. S. Sligh, Jr., and C. S. Cragoe. Scientific Paper of the Bureau

of Standards, No. 501. 110 pages, illustrations, plate, 8vo. Washington, Government Printing Office, 1925. Price, fifteen cents.

United States Department of Agriculture: Elimination of Waste Simplified Practice. Steel Reinforcing Bars. 8 pages, 8vo. Steel Lockers (Single and Double Tier). 8 pages, 8vo. Washington, Government Printing Office, 1925. Price, five cents each.

The Light Emitted by Tubes Containing Both Neon and Mercury Vapor, Along with the Liquid Metal. G. CLAUDE. (*Comptes Rendus,* March 23, 1925.)—Temperature has a considerable effect upon the quality of the light sent out by a mixture of neon and mercury vapor traversed by an electrical current, especially when the external diameter of the tube does not exceed 8 or 10 mm. "When the temperature is high, only the mercury spectrum appears. If the temperature is lowered progressively, some lines of neon are visible, then the light turns white, then rose, and finally red. This change manifestly comes about thus. As the tube cools down the tension of the mercury vapor diminishes step by step and the neon assumes more and more the task of transporting the current." With these ideas in mind the author constructed a tube with wide and narrow sections alternating, an electrical analogy to a chain of lakes joined by streams. He argued that in the constricted portions of the tube the temperature would be higher and in consequence the light from mercury would make its appearance, while in the wider and cooler parts the light of neon would show itself. Experiment, however, showed that the opposite took place. Under conditions not especially restricted, light from the mercury vapor alone was visible in the wide parts, while neon monopolized the emission of light in the narrow portions of the system.

The following experiment is valuable in getting an explanation of the unexpected results. In a tube of ordinary form that is emitting blue light, let the strength of the current be suddenly augmented. Then the light of neon springs into prominence, almost extinguishing that of mercury. "This effect is, however, fugitive. After a few seconds the stronger current volatilizes more mercury. This substance regains the upper hand and excludes the neon from light production. This shows us that a given mixture of neon and mercury has its mercury excited by a small density of current and has its neon excited by a high current density." In the case of the tube made up of wide and narrow sections, the temperature in the narrow parts is higher and more of the liquid mercury evaporates there. The tension of the vapor is, however, not permanently higher there than elsewhere in the composite tube, because the general tension is governed by that of the coldest part, which is the wide sections. There is thus established throughout the whole tube a certain pressure of mercury vapor. Where the current density is small, *i.e.,* in the wide sections, mercury light appears, and in the narrow parts with their high current density it is the neon that furnishes the light. The

author has thus, notwithstanding the early error of his reasoning, come upon a way of getting mercury light and neon light at the same time from a uniform mixture of the two radiating substances. A simple method of constructing the tube with wide and narrow parts is by inserting into a tube of uniform bore closely fitting sections of other tubing with narrow bore. By changing the lengths of these inserted sections the relative proportions of the two kinds of light will be varied and thus the resulting color will be controlled.

Within the past year the resignation of the distinguished author of this paper, perhaps best known for his work in the production of liquid air, from the reserve of the French army, was announced in the *Matin*. He had been assigned to duty in the selection of horses and objected to this diversion of his abilities. G. F. S.

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MODERN MILITARY ENGINEERING.*

BY

BRIGADIER-GENERAL EDGAR JADWIN.

Assistant Chief of Engineers, U. S. A.

MILITARY engineering may be defined as the art of so altering the theatre of war as to increase its strategic, tactical and logistic value. Strategy being the art of so directing campaigns as to gain maximum results from success while risking least harm in failure—Tactics the art of winning the battles required by strategy—Logistics the art of creating, training, transporting and maintaining the forces of war. The demand for it is evident throughout the fabric of military organization, from the front line elements in active contact with the enemy where military discipline and combat skill are paramount, thence, in a great war, through the vast communications zone or service of supply where the immediate needs of the fighting troops are cared for and where the military engineer does the bulk of his work, and finally in the heart of the nation itself, whence come all the elements of the country's military strength and where uninterrupted production is the first requirement. Military engineering is dependent vitally both on men and material. In the communications zone, military experience and discipline as well as technical ability are needed to provide all the utilities, communications and establishments required for the immediate support, maintenance and

* Address delivered Wednesday, September 17, 1924, on the occasion of the celebration of the centenary of the founding of The Franklin Institute.

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